

Fall 1997

# Thermodynamic properties of chlorocarbons and kinetic analysis for a- and b -addition of OH+C<sub>2</sub>H<sub>3</sub>CL

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## ABSTRACT

### THERMODYNAMIC PROPERTIES OF CHLOROCARBONS AND KINETIC ANALYSIS FOR $\alpha$ - AND $\beta$ -ADDITION OF OH + C<sub>2</sub>H<sub>3</sub>Cl

by  
Li Zhu

Thermodynamic properties,  $\Delta H_f^\circ$ ,  $S^\circ$  and  $C_p(T)$   $300 \leq T/K \leq 1500$ , for C<sub>1</sub>, C<sub>2</sub> chlorocarbons are calculated by AM1 and PM3 in MOPAC6, then compared with the literature data. AM1- and PM3-derived  $S^\circ$  and  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) are found to be consistent with the literature ( $R_d \leq \pm 5\%$ ).  $\Delta H_f^\circ$  of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>ClCH<sub>2</sub>Cl, CH<sub>2</sub>ClCHCl<sub>2</sub>, CHCl<sub>2</sub>CHCl<sub>2</sub>, and C<sub>2</sub>Cl<sub>4</sub> and C<sub>2</sub>Cl<sub>2</sub> calculated by PM3 as well as  $\Delta H_f^\circ$  of CCl<sub>4</sub>, C<sub>2</sub>HCl<sub>3</sub>, C<sub>2</sub>Cl<sub>4</sub> and C<sub>2</sub>Cl<sub>2</sub> by AM1 have more than  $\pm 5$  kcal/mol deviations. A Modified Group Additivity method is shown to be precise when compared with the literature.

A complete reaction system consisting of 12 elementary reaction and 19 species has been developed to model the reaction system of OH + C<sub>2</sub>H<sub>3</sub>Cl. There are two different carbon sites where addition can occur,  $\alpha$ -addition and  $\beta$ -addition, as well as two different abstractions,  $\alpha$ -abstraction and  $\beta$ -abstraction. Thermochemical kinetic parameters are developed for each elementary reaction and a chemical activation kinetic analysis using Multi-frequency QRRK theory for  $k(E)$  and modified strong collision approach for fall-off is used to calculate  $k$ 's as function of pressure and temperature. Thermodynamic parameters are determined by MOPAC6/PM3 and the Group Additivity estimation. We are trying to use ab initio and density function methods at different levels to calculate the addition reactants, products and the transition states. All reactions in the mechanism incorporate reverse reaction rates calculated from thermodynamic parameters and Microscopic Reversibility. Results show good agreement with several experimental data. Recommended rate constants for the primary addition channels at 760 torr are:  $k(\text{OH} + \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{CH}_2\text{OHC.HCl}) = 4.22 \times 10^{30} \times T^{-5.88} e^{4837/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ ,  $k(\text{OH} + \text{C}_2\text{H}_3\text{Cl} \rightarrow \text{Cl} + \text{CH}_2\text{CHOH}) = 8.61 \times 10^{12} \times T^{0.01} e^{4114/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ .

**THERMODYNAMIC PROPERTIES OF CHLOROCARBONS AND  
KINETIC ANALYSIS FOR  $\alpha$ - AND  $\beta$ -ADDITION OF OH + C<sub>2</sub>H<sub>3</sub>Cl**

by  
**Li Zhu**

**A Thesis  
Submitted to the Faculty of  
New Jersey Institute of Technology  
in Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Applied Chemistry**

**Department of Chemical Engineering,  
Chemistry, and Environmental Science**

**January 1998**

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APPROVAL PAGE

THERMODYNAMIC PROPERTIES OF CHLOROCARBONS AND  
KINETIC ANALYSIS FOR  $\alpha$ - AND  $\beta$ -ADDITION OF OH + C<sub>2</sub>H<sub>3</sub>Cl

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Li Zhu, Joseph W. Bozzelli and Tsan H. Lay,  
"Comparison of AM1 and PM3 in MOPAC6 with Literature for the Thermodynamic  
Properties of C<sub>1</sub>, C<sub>2</sub> Chlorocarbons." (In process of submission)



## ACKNOWLEDGMENT

I wish to express my appreciation to my advisor, Prof. Joseph W. Bozzelli, for his guidance, patience and encouragement throughout this research.

Special thanks to Professors Babara B. Kebbekus and Carol A. Venanzi for their help and suggestions.

I gratefully acknowledge funding from the New Jersey Institute of Technology NSF Industry/University Hazardous Substance Management Research Center grant number NJ 92-240050 and the USEPA-CalTech-MIT-NJIT Research Center on Airborne Organics grant number R819679.

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## **PART I**

### **COMPARISON OF AM1 AND PM3 IN MOPAC6 WITH LITERATURE FOR THE THERMODYNAMIC PARAMETERS OF C<sub>1</sub>, C<sub>2</sub> CHLOROCARBONS**

## CHAPTER 1

### PREFACE

Ideal gas thermodynamic properties,  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$  and  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) for 21  $C_1$  and  $C_2$  chlorocarbons are calculated using AM1 and PM3 in MOPAC6, then compared with the literature data. AM1- and PM3-derived  $S^\circ_{298}$  and  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) are found to be consistent with the literature data ( $R_d \leq \pm 5\%$ ) except  $C_p(300-500K)$  of  $C_2HCl$ ,  $C_2Cl_2$  and  $S^\circ_{298}$  of  $C_2HCl_5$ .  $\Delta H_f^\circ_{298}$  obtained by PM3 for some multichlorocarbons, such as  $CH_2Cl_2$ ,  $CH_2ClCH_2Cl$ ,  $CH_2ClCHCl_2$ ,  $CHCl_2CHCl_2$ ,  $C_2Cl_4$  and  $C_2Cl_2$ , are not in good agreement with the literature ( $D \geq \pm 5$  kcal/mol).  $\Delta H_f^\circ_{298}$  (kcal/mol) calculated by PM3 are corrected as following:  $\Delta H_f^\circ_{298,PM3} = -2.35 + 1.09 \times \Delta H_f^\circ_{298,literature}$  for the partially chlorinated  $C_1$  and  $C_2$  hydrocarbons;  $\Delta H_f^\circ_{298,PM3} = 5.36 + 1.07 \times \Delta H_f^\circ_{298,literature}$  for the fully Cl substituted  $C_1$  and  $C_2$  hydrocarbons.  $\Delta H_f^\circ_{298}$  of  $CCl_4$ ,  $C_2HCl_3$ ,  $C_2Cl_4$ ,  $C_2Cl_2$  obtained by AM1 have more than  $\pm 5$  kcal/mol deviations. A modified Group Additivity method is also used to calculate  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$  and  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) for the 21  $C_1$  and  $C_2$  chlorocarbons, and shown to be precise when compared with the literature. The use or application of AM1 and PM3 calculated  $\Delta H_f^\circ_{298}$  for chlorocarbons needs to include estimation of results due to the limited accuracy of the methods. We cautiously recommend use of modified Group Additivity as a method of thermodynamic property data estimation.



## CHAPTER 2

### INTRODUCTION

Chlorocarbons are widely used chemicals as solvents in syntheses, as cleaning agents and starting materials and in polymer, pesticide and other product manufacture. Chlorocarbons are present in the atmosphere, in both municipal and hazardous material combustion, as well as in destruction/cleanup process related to the above industrial applications. Thermodynamic properties of chlorocarbons are important to the industry and governmental agencies in analysis of environmental effects and in evaluation of kinetics for destruction and synthesis processes. There are a limited number of experimental studies on the thermodynamic properties data of chlorocarbons<sup>1-4</sup>. There are also several publications on estimation methods, or modification, evaluation of these methods.<sup>5-12</sup> Estimation techniques primarily include empirical or semiempirical methods, such as Group Additivity<sup>5-10</sup> or modified Group Additivity THERM (a computer code based on modified Group Additivity for chlorocarbons. See also 3.2 in Part I and Appendix)<sup>11,12</sup>, and MOPAC<sup>13-16</sup> semiempirical calculations. Group Additivity method<sup>5</sup> is to treat a molecular property as being composed of contributions due to groups. A group is defined as a polyvalent atom (ligancy  $\geq 2$ ) in a molecule together with all of its ligands. Semiempirical MOPAC and theoretical ab initio<sup>17-27</sup> are all molecular quantum-mechanical methods. Semiempirical methods such as MNDO<sup>13</sup>, AM1<sup>14</sup> and PM3<sup>15</sup> in MOPAC use a simpler Hamiltonian than the correct molecular Hamiltonian and use parameters whose values are adjusted to fit experimental data or the results of ab initio calculations. In contrast, high level ab initio calculation<sup>17-32</sup> use the correct Hamiltonian and does not use experimental data other than the values of the fundamental physical constants. Ab initio methods are

currently limited by computational cost as well as memory and scratch disk storage availability.

Group Additivity method of Benson<sup>5</sup> does not accurately treat multi chloro hydrocarbon molecules, and a set of added interaction parameters are needed<sup>10,33</sup>. Ab initio methods may be precise at higher levels but they are time-consuming and it is difficult to treat large systems.<sup>34</sup> High level theoretical calculations at MP2<sup>25,26</sup> or density function<sup>26</sup> levels are limited to about 6 or so Cl atoms. A method is clearly needed for providing accurate and convenient estimation of chlorocarbon and oxychlorocarbon species for multi carbon systems (3 carbons and higher). Semiempirical methods are faster than ab initio because some approximations and parameterizations are incorporated. Recently, Lay et al.<sup>35</sup> compared the enthalpies of formation (kcal/mol) of 10 cyclic oxygenated hydrocarbons and found a linear correction served to improve the PM3 values to within 3.2 kcal/mol: Experimental-determined Enthalpy =  $-1.642 + 0.882 \times \text{MOPAC6/PM3-determined enthalpy}$ ,  $R^2 = 0.993$ . The objective of this paper is to determine if MOPAC6 or a calibrated MOPAC6 calculation method is suitable for prediction of higher carbon number chlorocarbon species. We use AM1 and PM3 in MOPAC6 to obtain the thermodynamic quantities of C<sub>1</sub> and C<sub>2</sub> chlorocarbons, then compare with the respective values from literature<sup>1,2</sup> and THERM<sup>11,12</sup> (see 3.2 in Part I and Appendix).

## CHAPTER 3

### METHODOLOGY

#### 3.1 AM1 and PM3 in MOPAC6

AM1 and PM3 calculations in MOPAC6 are performed to obtain the thermodynamic parameters,  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ ,  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) on 21  $C_1$ ,  $C_2$  chlorocarbons, the results are given in Table IA. 1. For molecules having hindered rotors about C-C single bonds, i.e. saturated  $C_2$  chlorocarbons, the approximation method of Pitzer and Gwinn<sup>36</sup> is used to account for the internal rotor's contribution to the entropies and heat capacities. The two input parameters (Table IA. 2) for this calculation are determined as following: The reduced moments of inertia are calculated by  $\text{Moment} = \sum m_i \times r_i^2$ ; The barriers to free internal rotation are calculated by ab initio MP2/6-31G\* method (unpublished) and from literature when available<sup>3,5</sup>. PM3-determined moments of inertia, molecular geometries (bond lengths, angles, dihedral angles) and vibrational frequencies are given in Tables IA. 3, 4 and 5. Structures obtained by AM1 are similar to those obtained by PM3.

Available literature data on  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ ,  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) for  $C_1$ ,  $C_2$  chlorocarbons are listed in Table IA. 1, as well as the results of THERM (see 3.2 of Part I and Appendix). The differences of  $\Delta H_f^\circ_{298}$  among three literature, TRC<sup>1</sup>, JANAF<sup>2</sup> and SWS<sup>3</sup>, for some chlorocarbons are greater than  $\pm 1.0$  kcal/mol, such as  $CH_3Cl$ ,  $CCl_4$ ,  $CH_2ClCHCl_2$ ,  $C_2Cl_6$ ,  $C_2H_3Cl$ , E- and Z- $CHClCHCl$ . We choose TRC<sup>1</sup> and THERM results as references to represent the experimental values and evaluate literature data in our comparison with MOPAC6 AM1 and PM3. JANAF<sup>2</sup> data of chloroacetylenes are used for TRC data to compare with AM1 and PM3 since no TRC<sup>1</sup> data are available for chloroacetylenes.

Table IA. 1 Thermodynamic properties of C<sub>1</sub>, C<sub>2</sub> chlorocarbons

Molecule	ref.	$\Delta H_f^\circ$	$S^\circ$	Cp (T)						
				300K	400K	500K	600K	800K	1000K	1500K
CH <sub>3</sub> Cl	this work (AM1)	-18.95	55.88	9.69	11.52	13.25	14.37	17.07	18.85	21.69
	this work (PM3)	-14.68	56.02	9.91	11.70	13.37	14.80	17.08	18.82	21.65
	TRC <sup>1</sup>	-19.61	56.02	9.75	11.52	13.20	14.67	17.07	18.89	21.82
	JANAF <sup>2</sup>	-20.66	55.99	9.73	11.50	13.17	14.64	17.03	18.86	21.75
	SWS <sup>3</sup>	-20.63	56.04	9.77	11.52	13.19	14.66	17.04	18.86	
CH <sub>2</sub> Cl <sub>2</sub>	this work (AM1)	-25.85	64.22	12.03	14.21	16.00	17.39	19.42	20.82	22.94
	this work (PM3)	-17.14	64.78	12.59	14.67	16.34	17.66	19.58	20.93	22.99
	TRC <sup>1</sup>	-22.82	64.67	12.17	14.25	15.94	17.32	19.34	20.78	22.92
	JANAF <sup>2</sup>	-22.83	64.57	12.16	14.24	15.93	17.30	19.32	20.76	22.91
	SWS <sup>3</sup>	-22.80	64.59	12.26	14.46	15.87	17.36	19.38	20.80	
CHCl <sub>3</sub>	this work (AM1)	-29.00	70.00	15.27	17.51	19.14	20.32	21.87	22.85	24.18
	this work (PM3)	-20.87	71.21	16.34	18.37	19.81	20.83	22.20	23.07	24.29
	TRC <sup>1</sup>	-24.62	70.70	15.65	17.77	19.29	20.40	21.89	22.85	24.23
	JANAF <sup>2</sup>	-24.66	70.63	15.63	17.75	19.27	20.38	21.87	22.83	24.16
	SWS <sup>3</sup>	-24.20	70.66	15.76	17.83	19.34	20.44	21.91	22.86	
CCl <sub>4</sub>	this work (AM1)	-28.12	72.98	19.15	21.26	22.58	23.43	24.39	24.88	25.40
	this work (PM3)	-25.96	75.21	20.75	22.55	23.58	24.21	24.88	25.21	25.55
	TRC <sup>1</sup>	-22.92	74.14	19.96	21.94	23.11	23.84	24.66	25.07	25.53
	JANAF <sup>2</sup>	-22.94	74.02	19.93	21.92	23.09	23.82	24.64	25.05	25.47
	SWS <sup>3</sup>	-24.00	74.12	20.08	22.04	23.28	24.07	25.00	25.52	
C <sub>2</sub> H <sub>5</sub> Cl	*this work (AM1)	-26.16	65.66	14.57	18.07	21.24	23.90	28.02	31.07	35.86
	* this work (PM3)	-22.06	65.96	15.03	18.58	21.71	24.31	28.31	31.27	35.96
	TRC <sup>1</sup>	-26.86	65.97	14.98	18.56	21.68	24.30	28.41	31.46	36.24
	JANAF <sup>2</sup>	-26.80	66.01	15.03	18.57	21.61	24.22	28.37	31.44	36.16
	SWS <sup>3</sup>	-26.70	65.93	15.05	18.56	21.68	24.31	28.42	31.48	
	this work (THERM)	-27.00	66.26	14.93	18.38	21.48	24.10	28.17	31.24	
CH <sub>3</sub> CHCl <sub>2</sub>	*this work (AM1)	-31.10	72.32	17.74	21.38	24.44	26.89	30.54	33.14	37.14
	* this work (PM3)	-26.53	73.16	18.63	22.21	25.15	27.48	30.94	33.43	37.28
	TRC <sup>1</sup>	-31.13	72.98	18.26	21.86	24.81	27.21	30.82	33.43	37.44
	SWS <sup>3</sup>	-31.05	72.89	18.29	21.85	24.82	27.24	30.85	33.45	
	this work (THERM)	-31.10	73.05	18.40	21.82	24.67	27.15	30.69	33.35	
CH <sub>2</sub> ClCH <sub>2</sub> Cl	*this work (AM1)	-33.81	74.68	17.04	20.84	24.18	26.88	30.78	33.45	37.40
	* this work (PM3)	-24.68	75.23	17.68	21.50	24.77	27.38	31.16	33.74	37.57
	TRC <sup>1</sup>	-30.33	73.17	18.50	21.97	24.98	27.48	31.19	33.81	37.68
	SWS <sup>3</sup>	-31.00	73.66	19.00	22.00	24.70	26.90	30.40	33.00	
	this work (THERM)	-31.05	73.84	18.23	21.54	24.39	26.70	30.25	32.94	
CH <sub>3</sub> CCl <sub>3</sub>	*this work (AM1)	-31.92	76.44	21.64	25.04	27.69	29.78	32.84	34.99	38.25
	* this work (PM3)	-31.91	78.12	23.02	26.23	28.68	30.57	33.35	35.33	38.40
	TRC <sup>1</sup>	-34.04	76.56	22.09	25.74	28.55	30.71	33.78	35.84	38.84
	this work (THERM)	-33.90	76.55	22.02	25.70	28.65	30.89	34.08	35.98	
CH <sub>2</sub> ClCHCl <sub>2</sub>	*this work (AM1)	-37.22	82.18	20.16	24.06	27.29	29.83	33.40	35.72	38.89
	* this work (PM3)	-27.71	83.29	21.22	25.03	28.10	30.51	33.88	36.08	39.09
	TRC <sup>1</sup>	-34.83	79.77	20.31	24.49	27.77	30.32	33.88	36.18	39.33
	SWS <sup>3</sup>	-33.10	80.57	21.34	25.03	27.92	30.13	33.28	35.42	
	this work (THERM)	-34.00	81.43	21.53	24.85	27.39	29.55	32.58	35.05	
CH <sub>2</sub> ClCCl <sub>3</sub>	*this work (AM1)	-36.64	85.29	23.95	27.76	30.69	32.93	35.99	37.94	40.40
	*this work (PM3)	-31.90	87.38	25.47	29.06	31.75	33.78	36.56	38.34	40.61
	TRC <sup>1</sup>	-35.74	85.13	24.61	28.39	31.19	33.31	36.28	38.21	40.74
	this work (THERM)	-35.16	84.46	24.62	28.29	31.07	33.17	36.11	37.68	
CHCl <sub>2</sub> CHCl <sub>2</sub>	*this work (AM1)	-39.46	86.02	23.47	27.39	30.44	32.76	35.93	37.93	40.45
	*this work (PM3)	-30.11	88.34	24.85	28.56	31.39	33.53	36.46	38.33	40.67
	TRC <sup>1</sup>	-35.65	84.92	23.68	27.70	30.68	32.92	36.02	38.05	40.70
	SWS <sup>3</sup>	-36.50	86.69	24.16	27.90	30.77	32.91	35.85	37.76	
	this work (THERM)	-36.46	86.36	24.47	27.85	30.28	32.48	35.24	37.16	

Table IA. 1 Thermodynamic properties of C<sub>1</sub>, C<sub>2</sub> chlorocarbons (Continued)

Molecule	ref.	$\Delta H_f^\circ$	$S^\circ$	Cp (T)						
				300K	400K	500K	600K	800K	1000K	1500K
C <sub>2</sub> HCl <sub>5</sub>	*this work (AM1)	-38.02	93.65	27.28	31.09	33.85	35.84	38.40	39.97	41.90
	*this work (PM3)	-33.41	96.93	29.11	32.60	35.04	36.77	39.01	40.39	42.11
	TRC <sup>1</sup>	-34.83	91.25	28.25	31.99	34.55	36.38	38.75	40.21	42.03
	SWS <sup>3</sup>	-34.00	90.95	28.23	31.77	34.42	36.22	38.52	39.88	
	this work (THERM)	-34.00	90.95	28.49	31.86	34.21	36.02	38.20	39.79	
C <sub>2</sub> Cl <sub>6</sub>	*this work (AM1)	-35.78	95.39	31.23	34.94	37.39	39.03	40.97	42.02	43.17
	*this work (PM3)	-36.48	100.08	33.42	36.66	38.70	40.04	41.60	42.44	43.37
	TRC <sup>1</sup>	-33.23	95.39	32.71	36.24	38.44	39.86	41.52	42.42	43.35
	JANAF <sup>2</sup>	-32.08	95.07	33.21	36.68	38.78	40.14	41.71	42.55	43.37
	SWS <sup>3</sup>	-33.80	94.77	32.67	36.11	38.29	39.69	41.29	42.11	
	this work (THERM)	-34.06	94.77	32.72	36.16	38.35	39.76	41.39	42.42	
C <sub>2</sub> H <sub>3</sub> Cl	this work (AM1)	5.88	62.89	12.54	15.14	17.35	19.17	21.94	23.97	27.17
	this work (PM3)	9.72	63.13	13.01	15.65	17.83	19.60	22.29	24.26	27.37
	TRC <sup>1</sup>	6.81	63.15	12.82	15.55	17.78	19.60	22.35	24.36	27.46
	SWS <sup>3</sup>	8.40	63.08	12.89	15.56	17.80	19.61	22.35	24.35	
	this work (THERM)	5.06	63.01	13.00	15.56	17.81	19.70	22.37	24.37	
CH <sub>2</sub> CCl <sub>2</sub>	this work (AM1)	-0.05	68.43	15.53	18.22	20.29	21.91	24.27	25.92	28.39
	this work (PM3)	3.11	69.15	16.42	19.05	21.01	22.52	24.71	26.24	28.57
	TRC <sup>1</sup>	0.57	68.87	16.01	18.79	20.85	22.43	24.72	26.30	28.65
	SWS <sup>3</sup>	0.30	68.85	16.08	18.80	20.86	22.44	24.71	26.29	
	this work (THERM)	0.50	67.00	16.07	18.78	20.84	22.42	24.70	26.28	
Z-CHClCHCl	this work (AM1)	-3.31	69.06	15.06	17.82	20.01	21.72	24.18	25.87	28.39
	this work (PM3)	3.99	69.49	15.77	18.48	20.58	22.20	24.55	26.17	28.58
	TRC <sup>1</sup>	-0.67	69.28	15.55	18.40	20.56	22.23	24.61	26.24	28.64
	SWS <sup>3</sup>	0.45	69.20	15.61	18.41	20.57	22.23	24.60	26.23	
	this work (THERM)	0.00	69.25	16.26	18.97	21.08	22.72	24.79	26.17	
E-CHClCHCl	this work (AM1)	-3.43	69.11	15.42	17.96	20.06	21.73	24.17	25.86	28.38
	this work (PM3)	3.56	69.55	16.02	18.58	20.62	22.21	24.54	26.17	28.57
	TRC <sup>1</sup>	-0.10	69.34	15.92	18.57	20.65	22.28	24.63	26.25	28.64
	SWS <sup>3</sup>	1.00	69.29	15.99	18.58	20.65	22.28	24.62	26.24	
	this work (THERM)	0.30	69.25	16.45	19.01	21.05	22.68	24.79	26.20	
C <sub>2</sub> HCl <sub>3</sub>	this work (AM1)	-8.41	77.17	18.45	21.05	23.00	24.47	26.50	27.80	29.59
	this work (PM3)	-2.33	78.19	19.43	21.95	23.76	25.10	26.94	28.13	29.77
	TRC <sup>1</sup>	-2.30	77.77	19.20	21.83	23.71	25.10	26.98	28.18	29.82
	SWS <sup>3</sup>	-1.40	77.63	19.25	21.80	23.67	25.06	26.94	28.15	
	this work (THERM)	-2.22	77.67	19.26	21.80	23.67	25.06	26.94	28.11	
C <sub>2</sub> Cl <sub>4</sub>	this work (AM1)	-12.43	80.83	21.79	24.26	26.00	27.24	28.83	29.74	30.80
	this work (PM3)	-8.08	82.70	23.05	25.37	26.91	27.97	29.31	30.07	30.96
	TRC <sup>1</sup>	-2.90	81.54	22.70	25.13	26.75	27.89	29.31	30.10	31.00
	JANAF <sup>2</sup>	-2.97	82.05	22.84	25.19	26.78	27.91	29.30	30.09	30.98
	SWS <sup>3</sup>	-3.40	81.46	22.73	25.10	26.73	27.86	29.29	30.07	
	this work (THERM)	-3.15	81.47	22.73	25.10	26.72	27.86	29.28	30.02	
C <sub>2</sub> HCl	this work (AM1)	47.77	56.50	11.71	13.31	14.42	15.24	16.44	17.33	18.74
	this work (PM3)	46.57	56.54	11.80	13.39	14.50	15.32	16.53	17.41	18.81
	JANAF <sup>2</sup>	51.10	57.81	12.98	14.39	15.30	15.97	16.98	17.75	18.99
	this work (THERM)	51.42	58.10	13.18	14.39	15.19	15.87	16.87	17.56	
C <sub>2</sub> Cl <sub>2</sub>	this work (AM1)	41.59	62.99	14.80	16.05	16.90	17.53	18.43	19.04	19.88
	this work (PM3)	42.02	63.16	14.80	16.12	17.00	17.64	18.54	19.14	19.95
	JANAF <sup>2</sup>	50.10	65.01	15.80	16.86	17.69	18.31	19.13	19.60	20.20
	this work (THERM)	50.89	64.58	16.55	17.26	17.63	18.08	18.75	19.20	

\*:  $S^\circ$ <sub>298</sub>, Cp(T) from hindered internal rotations are included.Units of  $\Delta H_f^\circ$ <sub>298</sub>,  $S^\circ$ <sub>298</sub> and Cp(T) are kcal/mol, cal/mol.K and cal/mol.K, respectively.

**Table IA. 2** Reduced moments of inertia and rotational barriers

Internal Rotor in molecules	I <sub>a</sub> (amu x Å <sup>2</sup> )	I <sub>b</sub> (amu x Å <sup>2</sup> )	V (kcal/mol)	ref.
CH <sub>2</sub> Cl - CH <sub>3</sub>	103	3.2	3.70	Benson <sup>5</sup>
CHCl <sub>2</sub> - CH <sub>3</sub>	198	3.2	3.75	SWS <sup>3</sup>
CH <sub>2</sub> Cl - CH <sub>2</sub> Cl	102	102	5.42	MP2/6-31G*** <sup>a</sup>
CCl <sub>3</sub> - CH <sub>3</sub>	287	3.2	2.75	SWS <sup>3</sup>
CHCl <sub>2</sub> - CH <sub>2</sub> Cl	196	101	6.87	MP2/6-31G*** <sup>a</sup>
CCl <sub>3</sub> - CH <sub>2</sub> Cl	287	101	8.89	MP2/6-31G*** <sup>a</sup>
CHCl <sub>2</sub> - CHCl <sub>2</sub>	196	196	9.20	MP2/6-31G*** <sup>a</sup>
CCl <sub>3</sub> - CHCl <sub>2</sub>	288	196	12.66	MP2/6-31G*** <sup>a</sup>
CCl <sub>3</sub> - CCl <sub>3</sub>	288	288	15.00	Benson <sup>5</sup>

a: Unpublished work.

**Table IA. 3** Moments of inertia (10<sup>-47</sup> kg m<sup>2</sup>)

Molecule	I <sub>A</sub>	I <sub>B</sub>	I <sub>C</sub>	Molecule	I <sub>A</sub>	I <sub>B</sub>	I <sub>C</sub>
CH <sub>3</sub> Cl	5.32	62.55	62.55	C <sub>2</sub> H <sub>3</sub> Cl	27.45	148.43	165.35
CH <sub>2</sub> Cl <sub>2</sub>	28.57	240.44	263.66	CH <sub>3</sub> CHCl <sub>2</sub>	131.35	252.76	359.54
CHCl <sub>3</sub>	249.53	249.70	467.75	CH <sub>2</sub> ClCH <sub>2</sub> Cl	29.07	553.26	571.74
CCl <sub>4</sub>	478.84	478.86	478.98	CH <sub>3</sub> CCl <sub>3</sub>	350.75	350.79	482.34
C <sub>2</sub> H <sub>3</sub> Cl	15.12	133.87	148.99	CH <sub>2</sub> ClCHCl <sub>2</sub>	226.10	570.40	766.95
CH <sub>2</sub> CCl <sub>2</sub>	110.59	238.82	349.42	CH <sub>2</sub> ClCCl <sub>3</sub>	429.39	743.45	796.81
Z-CHClCHCl	74.15	302.58	376.73	CHCl <sub>2</sub> CHCl <sub>2</sub>	490.06	629.30	1091.50
E-CHClCHCl	16.11	529.03	545.14	C <sub>2</sub> HCl <sub>5</sub>	699.90	846.10	1100.79
C <sub>2</sub> HCl <sub>3</sub>	201.15	534.15	735.20	C <sub>2</sub> Cl <sub>6</sub>	956.80	1155.90	1155.92
C <sub>2</sub> Cl <sub>4</sub>	473.25	587.31	1060.56	C <sub>2</sub> HCl	0.00	140.38	140.38
				C <sub>2</sub> Cl <sub>2</sub>	0.00	566.34	566.34

Table IA. 4 PM3-calculated bond lengths, angles and dihedral angles

Molecule	Bond length (Å)	Bond angle (deg)	Dihedral angle (deg)	Molecule	Bond length (Å)	Bond angle (deg)	Dihedral angle (deg)	Molecule	Bond length (Å)	Bond angle (deg)	Dihedral angle (deg)
CH <sub>3</sub> Cl				CH <sub>3</sub> CCl <sub>3</sub>				C <sub>2</sub> H <sub>3</sub> Cl			
C1-H1	1.094			C1-C2	1.501			C1-C2	1.326		
C1-H2	1.094	109.1		C1-C11	1.759	111.0		C1-C11	1.689	121.0	
C1-H3	1.094	109.1	119.1	C1-C12	1.760	110.8	119.9	C1-H1	1.095	123.5	180.0
C1-Cl1	1.765	109.8	120.4	C1-C13	1.759	111.0	119.9	C2-H2	1.086	123.2	180.0
CH <sub>2</sub> Cl <sub>2</sub>				C2-H1	1.098	111.1	179.9	C2-H3	1.086	122.4	-180.0
C1-H1	1.103			C2-H2	1.098	111.1	-120.0	CH <sub>2</sub> CCl <sub>2</sub>			
C1-H2	1.102	108.4		C2-H3	1.098	111.1	-120.0	C1-C2	1.329		
C1-Cl1	1.758	110.1	120.5	CH <sub>2</sub> ClCHCl <sub>2</sub>				C1-Cl1	1.682	122.7	
C1-Cl2	1.758	110.1	118.8	C1-C2	1.506			C1-Cl2	1.682	122.7	180.0
CHCl <sub>3</sub>				C1-C11	1.769	109.3		C2-H1	1.086	122.5	-180.0
C1-H1	1.111			C1-C12	1.764	110.1	117.4	C2-H2	1.086	122.5	-180.0
C1-Cl1	1.752	110.4		C1-H1	1.113	111.8	121.6	Z-CHClCHCl			
C1-Cl2	1.753	110.2	119.9	C2-Cl3	1.772	108.9	52.76	C1-C2	1.334		
C1-Cl3	1.752	110.4	119.9	C2-H2	1.105	110.9	-120.0	C1-Cl1	1.678	121.4	
CCl <sub>4</sub>				C2-H3	1.105	111.5	-120.0	C1-H1	1.096	122.2	180.0
C1-Cl1	1.747			CH <sub>2</sub> ClCCl <sub>3</sub>				C2-Cl2	1.678	121.4	-180.0
C1-Cl2	1.746	109.5		C1-C2	1.506			C2-H2	1.096	122.2	-180.0
C1-Cl3	1.747	109.4	120.0	C1-C11	1.755	110.8		E-CHClCHCl			
C1-Cl4	1.746	109.5	120.0	C1-C12	1.755	110.8	120.5	C1-C2	1.333		
C <sub>2</sub> H <sub>5</sub> Cl				C1-C13	1.760	110.1	119.8	C1-Cl1	1.681	120.6	
C1-C2	1.502			C2-Cl4	1.768	109.1	180.0	C1-H1	1.096	123.0	180.0
C1-Cl1	1.782	109.0		C2-H1	1.105	110.9	-120.4	C2-H2	1.096	123.0	180.0
C1-H1	1.104	112.1	119.6	C2-H2	1.105	110.9	-119.3	C2-Cl2	1.681	120.6	-180.0
C1-H2	1.104	112.0	120.7	CHCl <sub>2</sub> CHCl <sub>2</sub>				C <sub>2</sub> HCl <sub>3</sub>			
C2-H3	1.098	111.6	-179.7	C1-C2	1.509			C1-C2	1.337		
C2-H4	1.098	111.0	-120.0	C1-Cl1	1.764	109.4		C1-Cl1	1.674	122.5	
C2-H5	1.098	111.6	-120.0	C1-Cl2	1.764	109.4	117.5	C1-Cl2	1.677	121.9	-179.9
CH <sub>3</sub> CHCl <sub>2</sub>				C1-H1	1.114	111.5	121.2	C2-Cl3	1.672	121.0	-179.9
C1-C2	1.502			C2-Cl3	1.763	109.5	58.6	C2-H1	1.096	122.0	-180.0
C1-Cl1	1.770	109.9		C2-Cl4	1.764	109.4	-117.5	C <sub>2</sub> Cl <sub>4</sub>			
C1-Cl2	1.770	109.9	117.3	C2-H2	1.114	111.4	-121.2	C1-C2	1.345		
C1-H1	1.112	112.3	121.4	C <sub>2</sub> HCl <sub>3</sub>				C1-Cl1	1.670	121.9	
C2-H2	1.098	111.6	180.8	C1-C2	1.511			C1-Cl2	1.670	121.9	179.8
C2-H3	1.098	111.1	-120.0	C1-Cl1	1.757	110.2		C2-Cl3	1.670	121.9	179.8
C2-H4	1.098	111.1	-119.9	C1-Cl2	1.753	110.7	120.2	C2-Cl4	1.670	121.9	-179.8
CH <sub>2</sub> ClCH <sub>2</sub> Cl				C1-Cl3	1.756	110.2	120.2	C <sub>2</sub> HCl			
C1-C2	1.505			C2-Cl4	1.760	109.5	179.1	C1-C2	1.190		
C1-Cl1	1.776	108.6		C2-Cl5	1.761	109.5	-118.0	C1-Cl1	1.664	180.0	
C1-H1	1.104	111.7	120.1	C2-H1	1.113	110.7	-121.0	C2-H1	1.064	180.0	0.0
C1-H2	1.105	111.6	119.9	C <sub>2</sub> Cl <sub>6</sub>				C <sub>2</sub> Cl <sub>2</sub>			
C2-Cl2	1.776	108.6	179.9	C1-C2	1.512			C1-C2	1.190		
C2-H3	1.105	111.6	-119.9	C1-Cl1	1.754	110.2		C1-Cl1	1.664	180.0	
C2-H4	1.104	111.8	-120.1	C1-Cl2	1.754	110.1	120.0	C2-Cl2	1.664	180.0	0.0
				C1-Cl3	1.754	110.2	120.0				
				C2-Cl4	1.754	110.2	179.9				
				C2-Cl5	1.754	110.1	-120.0				
				C2-Cl6	1.754	110.2	-120.0				

Table IA. 5 PM3-calculated vibrational frequencies of C<sub>1</sub>, C<sub>2</sub> chlorocarbons

Molecule	Frequencies (cm <sup>-1</sup> )
CH <sub>3</sub> Cl	676 1007 1007 1344 1383 1383 3125 3125 3195
CH <sub>2</sub> Cl <sub>2</sub>	274 660 670 888 1090 1218 1353 3033 3076
CHCl <sub>3</sub>	240 240 347 637 661 662 1146 1146 2966
CCl <sub>4</sub>	195 195 284 284 284 458 670 670 671
C <sub>2</sub> H <sub>3</sub> Cl	164 337 634 820 1014 1033 1127 1136 1254 1366 1395 1403 1421 3009 3067 3087 3087 3184
CH <sub>3</sub> CHCl <sub>2</sub>	147 258 300 399 622 625 1001 1018 1126 1161 1218 1385 1393 1394 2952 3085 3087 3180
CH <sub>2</sub> ClCH <sub>2</sub> Cl	60 225 290 690 739 788 975 1062 1124 1127 1204 1298 1364 1400 2999 3011 3063 3065
CH <sub>3</sub> CCl <sub>3</sub>	135 218 218 320 322 323 522 632 633 1027 1028 1180 1380 1381 1382 3086 3087 3177
CH <sub>2</sub> ClCHCl <sub>2</sub>	171 237 316 378 622 687 741 923 1073 1119 1151 1183 1283 1370 2947 3001 3059
CH <sub>2</sub> ClCCl <sub>3</sub>	127 208 216 287 312 355 533 630 689 759 935 1083 1149 1264 1358 3000 3056
CHCl <sub>2</sub> CHCl <sub>2</sub>	117 183 272 280 311 358 683 688 731 746 1109 1124 1141 1158 1260 2939 2945
C <sub>2</sub> HCl <sub>3</sub>	116 139 181 206 251 305 306 387 548 683 686 754 762 1112 1147 1223 2943
C <sub>2</sub> Cl <sub>6</sub>	113 116 178 181 181 242 243 320 321 348 431 663 688 688 776 777 1189
C <sub>2</sub> H <sub>3</sub> Cl	391 594 654 907 996 1024 1190 1303 1805 3069 3141 3148
CH <sub>2</sub> CCl <sub>2</sub>	285 348 463 572 607 686 1013 1023 1292 1798 3140 3146
Z-CHClCHCl	156 358 528 661 763 796 944 1163 1202 1781 3059 3079
E-CHClCHCl	201 240 335 764 798 888 895 1163 1195 1783 3064 3068
C <sub>2</sub> HCl <sub>3</sub>	148 185 263 368 469 591 771 840 874 1180 1771 3066
C <sub>2</sub> Cl <sub>4</sub>	89 129 202 295 305 327 438 586 737 799 883 1758
C <sub>2</sub> HCl	395 395 760 844 844 2232 3356
C <sub>2</sub> Cl <sub>2</sub>	196 197 484 500 500 1009 2312

### 3.2 Modified Group Additivity: THERM

We have developed a new, unique set of chlorocarbon groups plus interaction terms (Table IA. 6) for use by Group Additivity to estimate the thermodynamic properties of chlorocarbon molecules and daughter radicals (here daughter signifies the parent molecule with a hydrogen atom removed from central atom). This is because most groups needed for chlorocarbon or oxygenated chlorocarbons do not exist in the literature, and current Benson group additivity does not work to a reasonable accurate degree (it is not accurate



to within  $\pm 3$  kcal/mol for chlorocarbons). We have developed chlorocarbon groups by taking a core set of literature experimental data for chlorocarbons plus a specific, consistent definition for each chlorocarbon group in the derivation for use in Group Additivity. This when combined with a set of interaction terms leads to accurate calculation of chlorocarbon thermodynamic parameters. Fluorocarbon groups are derived in a similar manner.

Correct definition of initial groups is important to development of a Group Additivity scheme for accurate property estimation. Group Additivity is known to work well for hydrocarbons with Gauche interaction terms.<sup>5</sup> Chlorocarbon groups are therefore derived from the experimental thermodynamic property data on respective chlorinated hydrocarbons. These groups are defined by use of groups where there are only carbon or hydrogen atoms on adjacent carbons. For examples the C/C/Cl/H<sub>2</sub>, C/C/Cl<sub>2</sub>/H or C/C/Cl<sub>3</sub> groups are derived from chloroethane (CH<sub>3</sub>-CH<sub>2</sub>Cl); 1,1-dichloroethane (CH<sub>3</sub>CHCl<sub>2</sub>); and 1,1,1-trichloroethane (CH<sub>3</sub>CCl<sub>3</sub>), respectively. There are no chlorines on the carbon atoms adjacent to the carbon atoms containing the chlorines. The C/C/Cl<sub>3</sub> group, for example, is defined from the parent 1,1,1-trichloroethane, and the C/C/H<sub>3</sub> group. Thermodynamic properties of chlorocarbons with no Cl or F on the carbon atoms adjacent a carbon with Cl are now accurately predicted, but an adjustment needs to be made for chlorocarbon or fluoro-chloro carbon species where there is a Cl or F on an adjacent carbon, such as 1,2-dichloroethane or 1,1,2-trichloroethylene. This adjustment comes in the form of an interaction group to count the total number of Cl atoms (that interact) on the two adjacent carbons. There is no interaction group when the Cl atoms are only on one of two adjacent carbons.

**Table IA. 6** Selected chlorocarbon groups and interaction groups for multi chloro-alkanes, alkenes and alkynes<sup>a</sup>

Group	$\Delta H_f^\circ_{298}$	$S^\circ_{298}$	Cp(T)					
			300K	400K	500K	600K	800K	1000K
C/C/Cl/H <sub>2</sub>	-16.80	38.03	8.74	10.54	12.08	13.31	15.15	16.47
C/C/Cl <sub>2</sub> /H	-21.04	44.91	11.99	13.98	15.53	16.62	18.09	18.80
C/C/Cl <sub>3</sub>	-23.84	50.69	15.83	17.86	19.25	20.10	21.06	21.21
C <sub>D</sub> /Cl/H	-1.20	35.40	7.90	9.20	10.30	11.20	12.30	13.10
C <sub>D</sub> /Cl <sub>2</sub>	-5.76	40.77	10.97	12.42	13.33	13.92	14.63	15.01
C <sub>T</sub> /H	27.25	24.70	5.28	5.99	6.49	6.87	7.47	7.96
C <sub>T</sub> /Cl	24.17	33.40	7.90	8.40	8.70	9.00	9.40	9.60
INT/Cl <sub>2</sub>	2.55	-0.84	0.75	0.46	0.23	0.08	-0.05	-0.05
INT/Cl <sub>3</sub>	3.70	-1.42	0.58	0.33	0.04	-0.12	-0.24	-0.24
INT/Cl <sub>4</sub>	5.34	-1.90	0.05	-0.11	-0.26	-0.24	-0.10	0.43
INT/Cl <sub>5</sub>	10.60	-2.20	0.45	0.02	-0.31	-0.44	-0.53	0.02
INT/Cl <sub>6</sub>	13.34	-0.51	1.06	0.44	-0.15	-0.44	-0.73	-0.17
INT/C <sub>D</sub> /Cl <sub>2</sub>	2.70	-0.17	0.65	0.61	0.45	0.28	0.19	0.15
INT/C <sub>D</sub> /Cl <sub>3</sub>	4.74	1.50	0.39	0.18	0.04	-0.06	0.01	0.04
INT/C <sub>D</sub> /Cl <sub>4</sub>	8.37	2.68	0.79	0.26	0.06	0.02	0.02	0.05

a: Only chlorocarbon groups used in this work are listed.

Units of  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$  and Cp(T) are kcal/mol, cal/mol.K and cal/mol.K, respectively.

THERM (modified Group Additivity) files for the 17 chlorocarbons discussed in this work are attached as Appendix.

## CHAPTER 4

### RESULTS

#### 4.1 Enthalpy

$\Delta H_f^\circ_{298}$  for  $C_1$ ,  $C_2$  chlorocarbons from PM3 (or AM1), TRC<sup>1</sup> and THERM are compared in Figures IB. 1 to 6. Each class of chlorocarbons (saturated  $C_1$ , saturated  $C_2$ ,  $C_2$  containing carbon-carbon double bonds and  $C_2$  containing carbon-carbon triple bonds) are shown in different legends.

Data in Table IA. 1 illustrates that the deviations of  $\Delta H_f^\circ_{298}$  between AM1 and TRC data range from -9.53 kcal/mol ( $C_2Cl_4$ ) to -5.20 kcal/mol ( $CCl_4$ ). Four compounds have more than  $\pm 5$  kcal/mol deviations, i.e.  $CCl_4$ ,  $C_2HCl_3$ ,  $C_2Cl_4$ ,  $C_2Cl_2$ . The deviations of  $\Delta H_f^\circ_{298}$  between PM3 and TRC data are within +7.12 kcal/mol ( $CH_2ClCHCl_2$ ) and -8.08 kcal/mol ( $C_2Cl_4$ ). Six compounds have more than  $\pm 5$  kcal/mol deviations, i.e.  $CH_2Cl_2$ ,  $CH_2ClCH_2Cl$ ,  $CH_2ClCHCl_2$ ,  $CHCl_2CHCl_2$ ,  $C_2Cl_4$  and  $C_2Cl_2$ . It is seen from the comparison of Figures IB. 1, 3 and Figures IB. 2, 4 that AM1 is better than PM3 for predicting  $\Delta H_f^\circ_{298}$  of  $C_1$ ,  $C_2$  saturated chlorocarbons.

Statistics in Figures IB. 3 and 4 indicate that  $\Delta H_f^\circ_{298}$  for all  $C_1$ ,  $C_2$  chlorocarbons between PM3 and TRC or PM3 and modified Group Additivity (THERM) do not have a good linear relationship:  $R^2$  factors are 0.980 and 0.984, respectively. An important observation is that the each class of chlorocarbons has similar, local non linearity: PM3 consistently predicts  $\Delta H_f^\circ_{298}$  of the fully chlorinated hydrocarbons to be too low. For examples, PM3-determined  $\Delta H_f^\circ_{298}$  of  $CCl_4$ ,  $C_2Cl_6$ ,  $C_2Cl_4$  and  $C_2Cl_2$  to be 3.04, 3.25, 5.18, 8.08 kcal/mol lower than experimental data, respectively. Two types of these  $C_1$ ,  $C_2$  chlorocarbons are separately considered: (i) the fully chlorinated and (ii) the partially

chlorinated hydrocarbons (containing one or more C-H bond). Comparisons of the separate fits to the literature data are plotted in Figures IB. 5, 6 and show much better linearity. This suggests that PM3 under-predicts Gauche interactions or Cl-Cl interactions. Conventional Gauche interactions<sup>5</sup> are not appropriate for chlorocarbon species and a series of new interaction terms are developed.<sup>10,33</sup> Figures IB. 5 and 6 suggest, in part, the correction terms to the PM3 calculated  $\Delta H_f^\circ_{298}$  (in kcal/mol) for the respective TRC and THERM data as following:

$$\Delta H_f^\circ_{298,PM3} = -2.35 + 1.09 \times \Delta H_f^\circ_{298,literature} \text{ for the partially chlorinated hydrocarbons;}$$

$$\Delta H_f^\circ_{298,PM3} = 5.36 + 1.07 \times \Delta H_f^\circ_{298,literature} \text{ for the fully chlorinated hydrocarbons;}$$

$$\Delta H_f^\circ_{298,PM3} = -2.19 + 1.08 \times \Delta H_f^\circ_{298,THERM} \text{ for the partially chlorinated hydrocarbons;}$$

$$\Delta H_f^\circ_{298,PM3} = 5.48 + 1.08 \times \Delta H_f^\circ_{298,THERM} \text{ for the fully chlorinated hydrocarbons.}$$

To estimate higher carbon number chlorocarbons ( $C_n$ ,  $n \geq 3$ ), we define on extension of these two types of chlorocarbons: (i) the fully chlorinated and (ii) the partially chlorinated hydrocarbon species.

Table IA. 1 shows that modified Group Additivity (THERM) is consistent with the literature. Deviations of  $\Delta H_f^\circ_{298}$  between literature and THERM are within  $\pm 1$  kcal/mol for all 17  $C_2$  chlorocarbons except  $C_2H_3Cl$  (+1.75 kcal/mol).

## 4.2 Entropy

Comparisons of  $S^\circ_{298}$  for  $C_1$ ,  $C_2$  chlorocarbons are shown in Figures IB. 7 to 10 for data from TRC and THERM, respectively. Relative deviations between AM1 and TRC are all less than  $\pm 5\%$ . Deviations between PM3 and TRC range from -1.85 cal/mol.K ( $C_2Cl_2$ ) to

+5.68 cal/mol.K ( $C_2HCl_3$ ), relative deviations are all less than  $\pm 5\%$  except  $C_2HCl_3$  (6.2%) and most are within  $\pm 2\%$ . The slopes greater than 0.85 and  $R^2$ 's greater than 0.993 (Figures IB. 7 to 10) indicate that the AM1 or PM3 data are sufficiently accurate for estimation of the standard entropies of chlorocarbons. THERM results of  $S^\circ_{298}$  in Table IA. 1 are in good agreement with the literature. Relative deviations of  $S^\circ_{298}$  between THERM and TRC are less than  $\pm 2\%$  for all  $C_1$ ,  $C_2$  chlorocarbons

### 4.3 Heat Capacity

Figures IB. 11 to 14 show comparison of MOPAC6-derived  $Cp_{300}$  with the literature values, where all the deviations between AM1 or PM3 and TRC are less than  $\pm 1.5$  cal/mol.K. Relative deviations are all within  $\pm 5\%$  except  $CH\equiv CCl$  (-9.8%) and  $CCl\equiv CCl$  (-6.3%). Figures IB. 11 and 13 show that the slopes are greater than 0.94 and  $R^2$  factors are greater than 0.992 for all  $C_1$ ,  $C_2$  chlorocarbons. The agreements of AM1 or PM3 calculation with literature data indicate that AM1 and PM3 can be useful in estimation  $Cp(T)$ , providing account of internal rotations is included when appropriate. Relative deviations of  $Cp(T)$  between THERM and TRC less than  $\pm 1.2\%$  for all  $C_2$  chlorocarbons show that THERM-calculated  $Cp(T)$  are consist well with literature data.

The AM1 and PM3 calculations are satisfactory for  $Cp(T)$  ( $400 \leq T/K \leq 1500$ ) of chloromethanes, chloroethanes and chloroethenes since relative deviations of AM1 and PM3  $Cp(T)$  ( $400 \leq T/K \leq 1500$ ) compared with literature are all within  $\pm 5\%$  and most are less than  $\pm 1\%$ .  $Cp(T)$  of  $CH\equiv CCl$  and  $CCl\equiv CCl$  have more than  $\pm 5\%$  of relative deviations at 300-500 K.

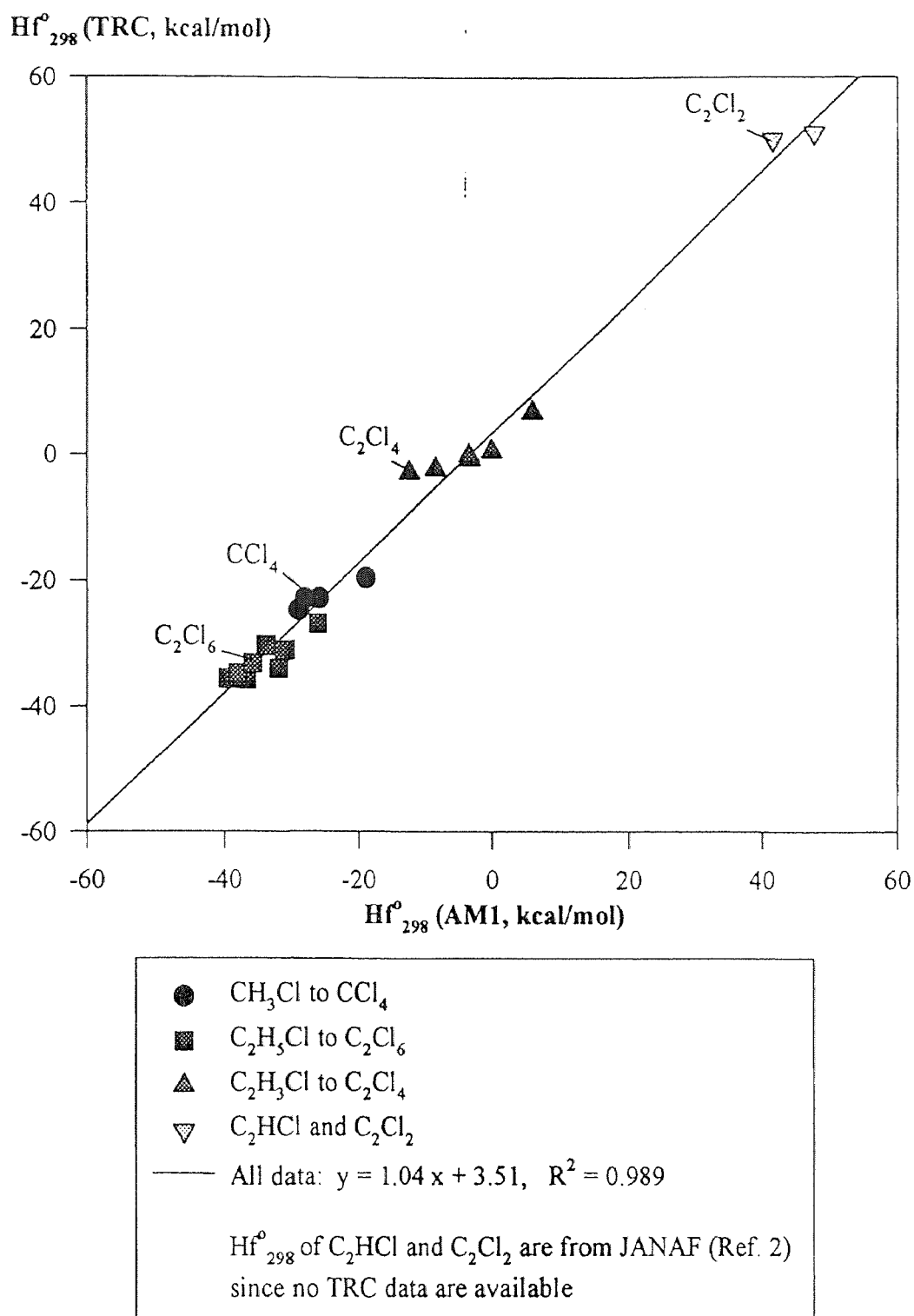


Figure IB. 1 Comparison of  $Hf_{298}^{\circ}$ : TRC vs. AM1

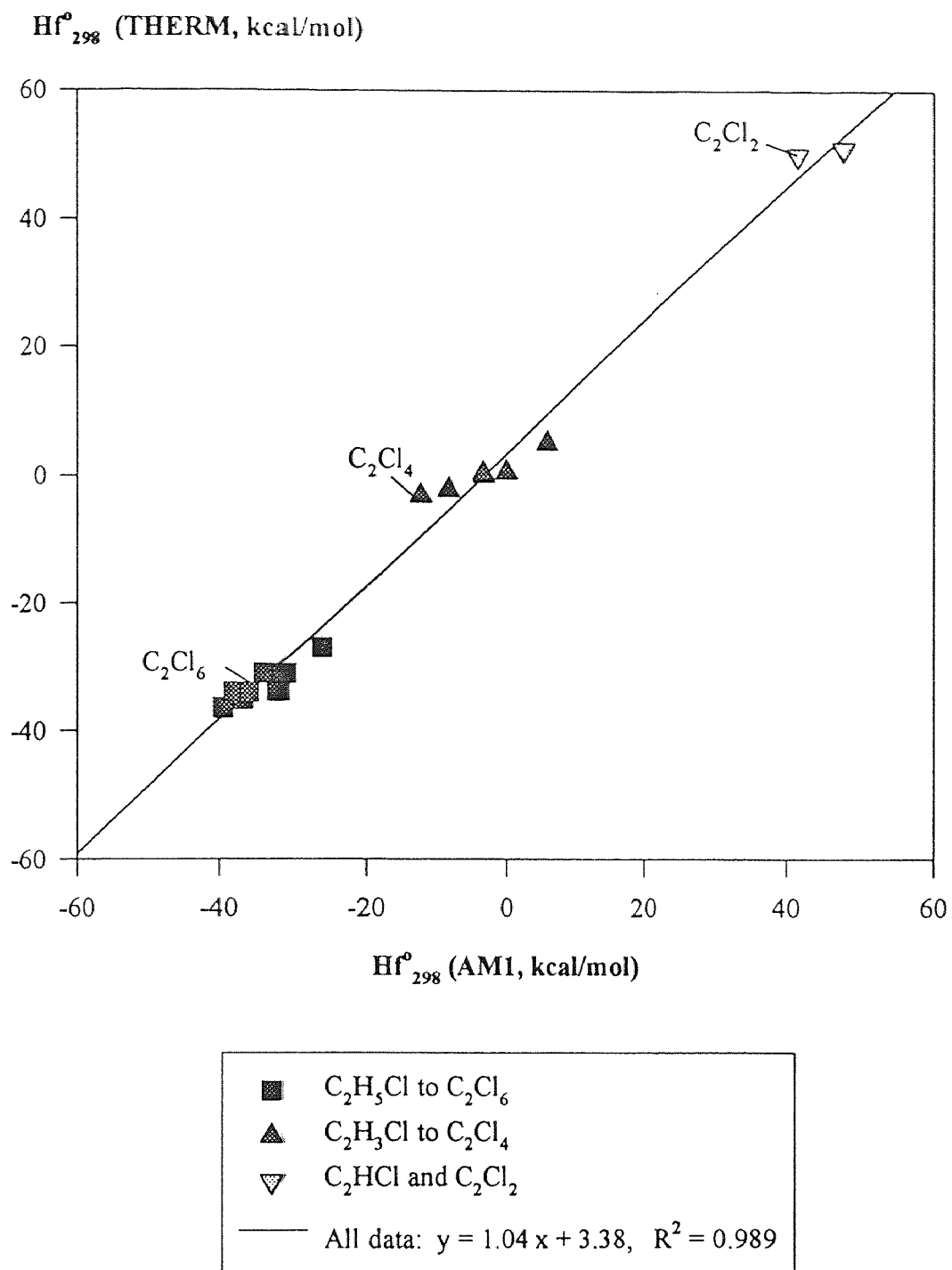


Figure IB. 2 Comparison of  $Hf_{298}^\circ$ : THERM vs. AM1

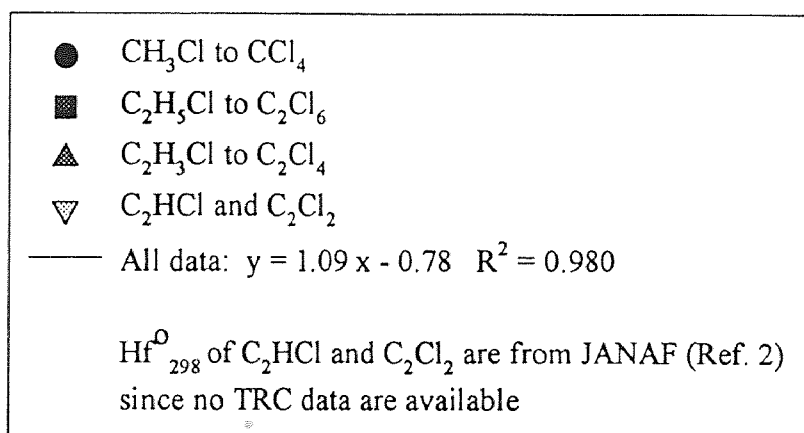
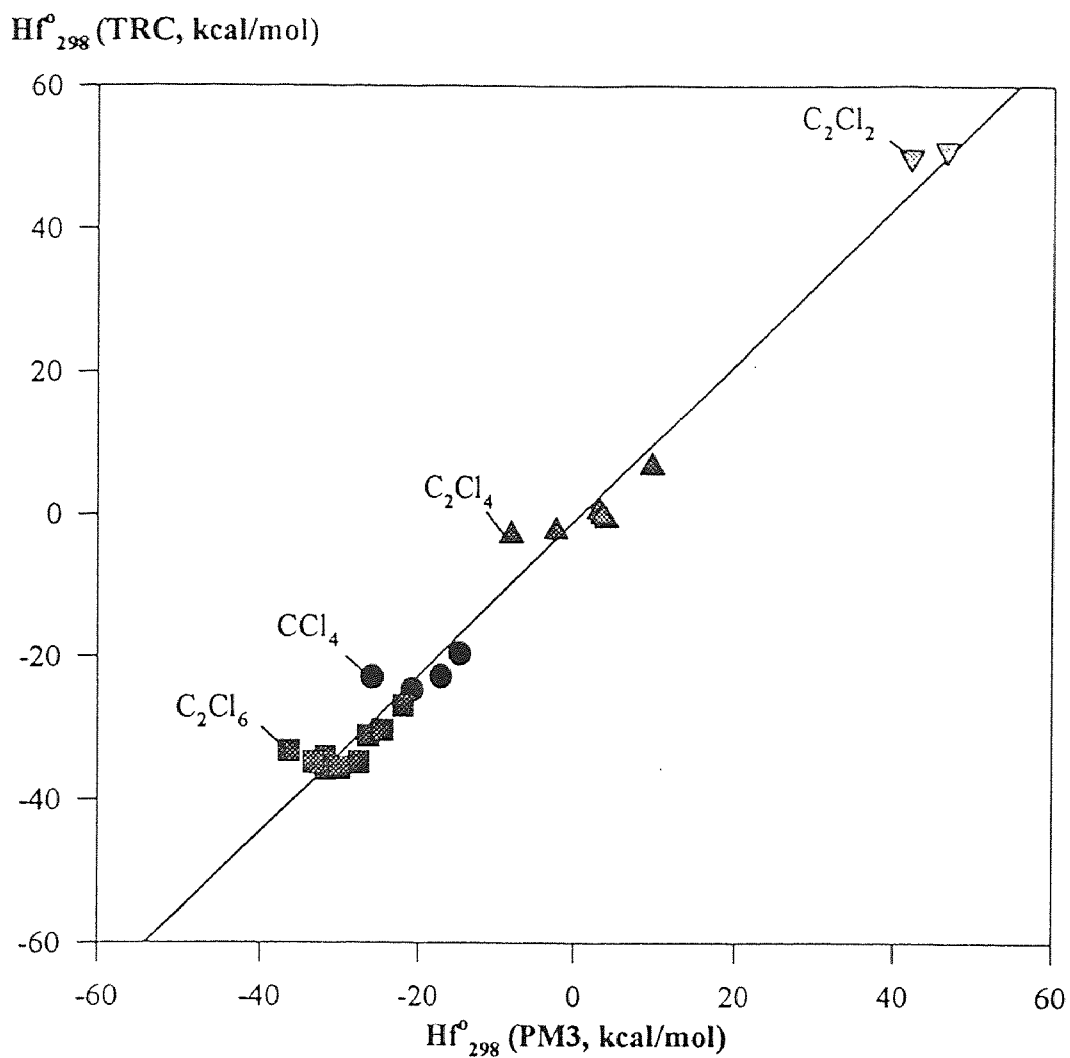


Figure IB. 3 Comparison of  $Hf^{\circ}_{298}$ : TRC vs. PM3



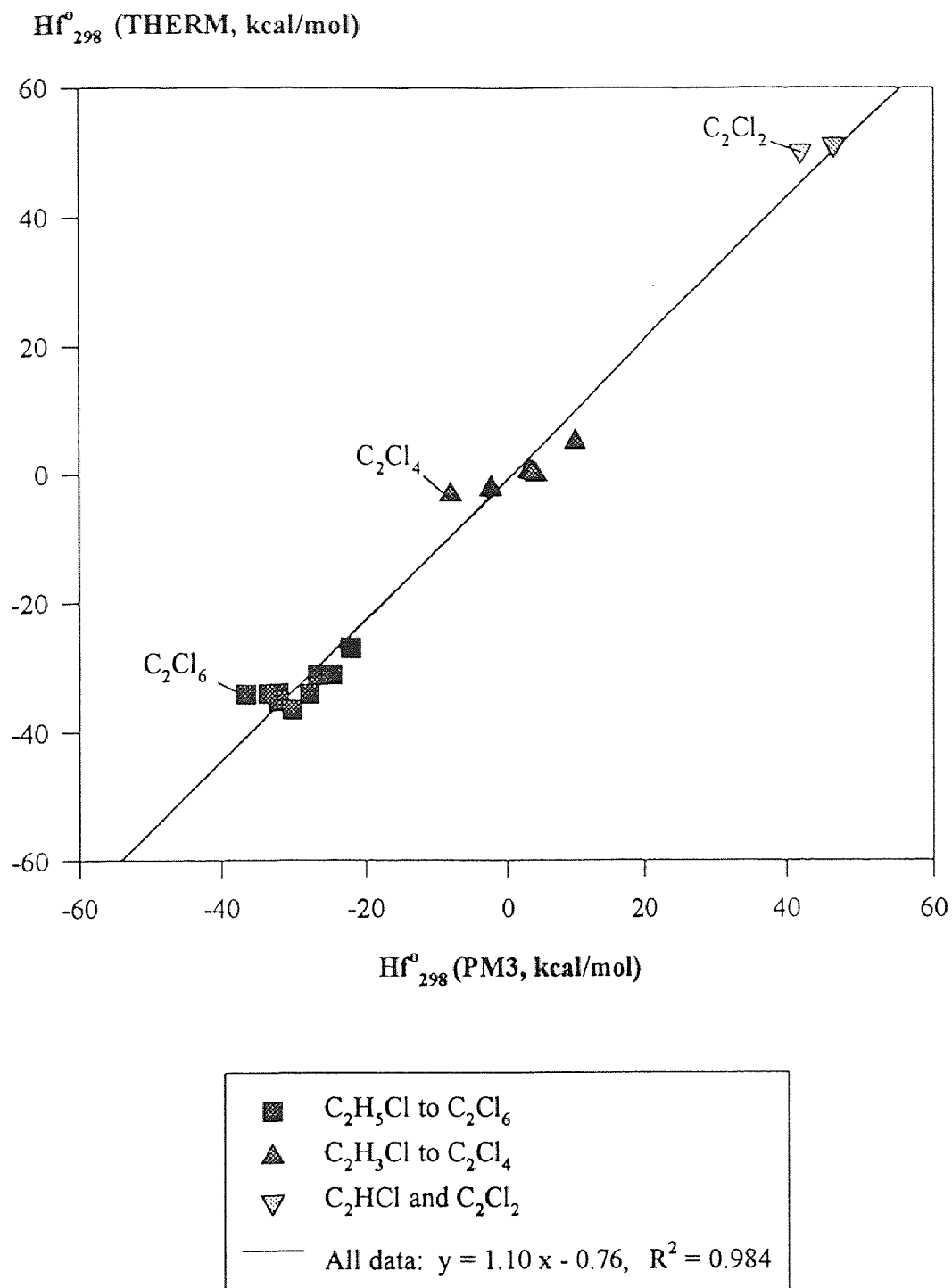


Figure IB. 4 Comparison of  $Hf_{298}^{\circ}$ : THERM vs. PM3

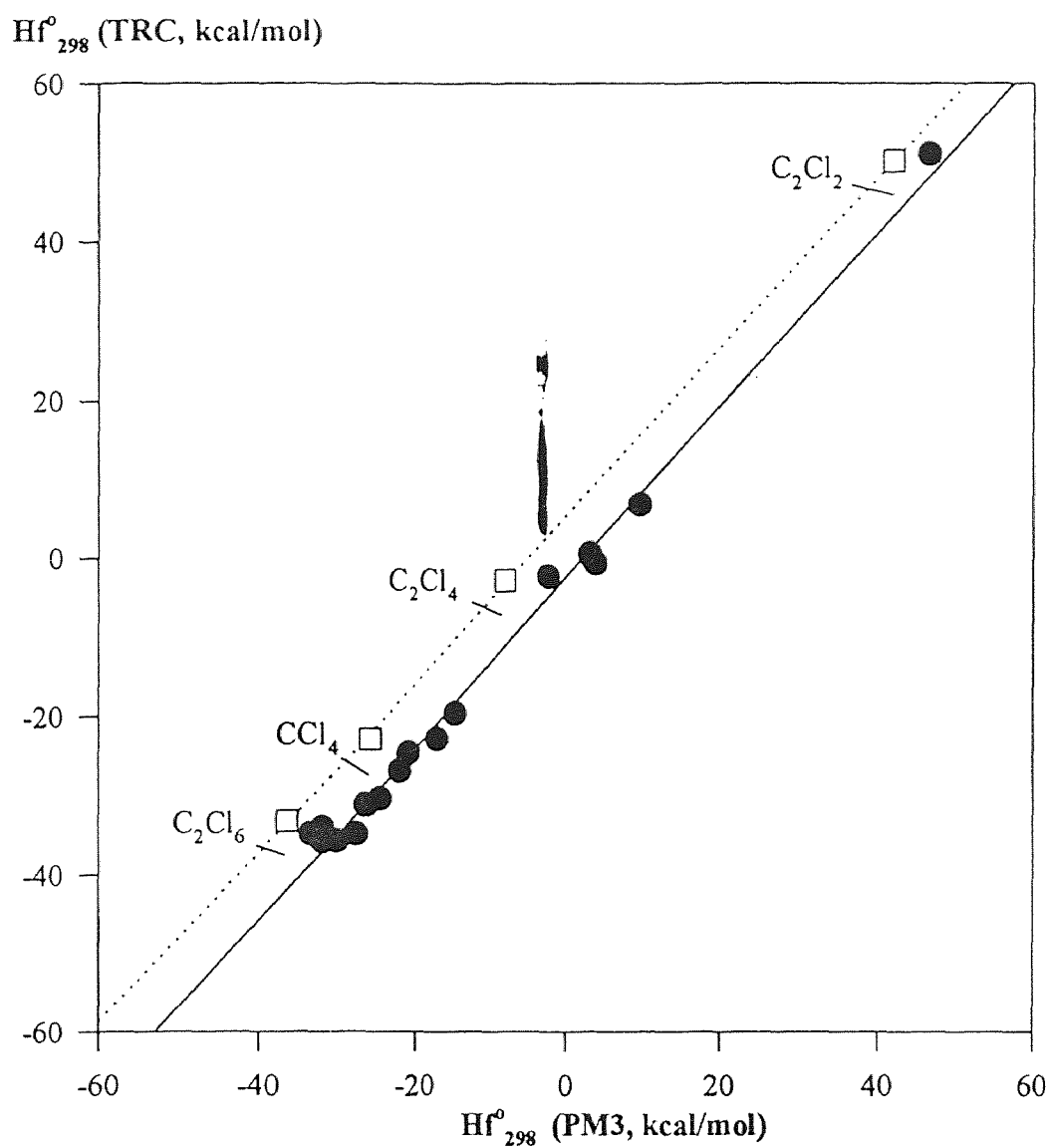


Figure IB. 5 Comparison of  $Hf_{298}^{\circ}$ : TRC vs. PM3

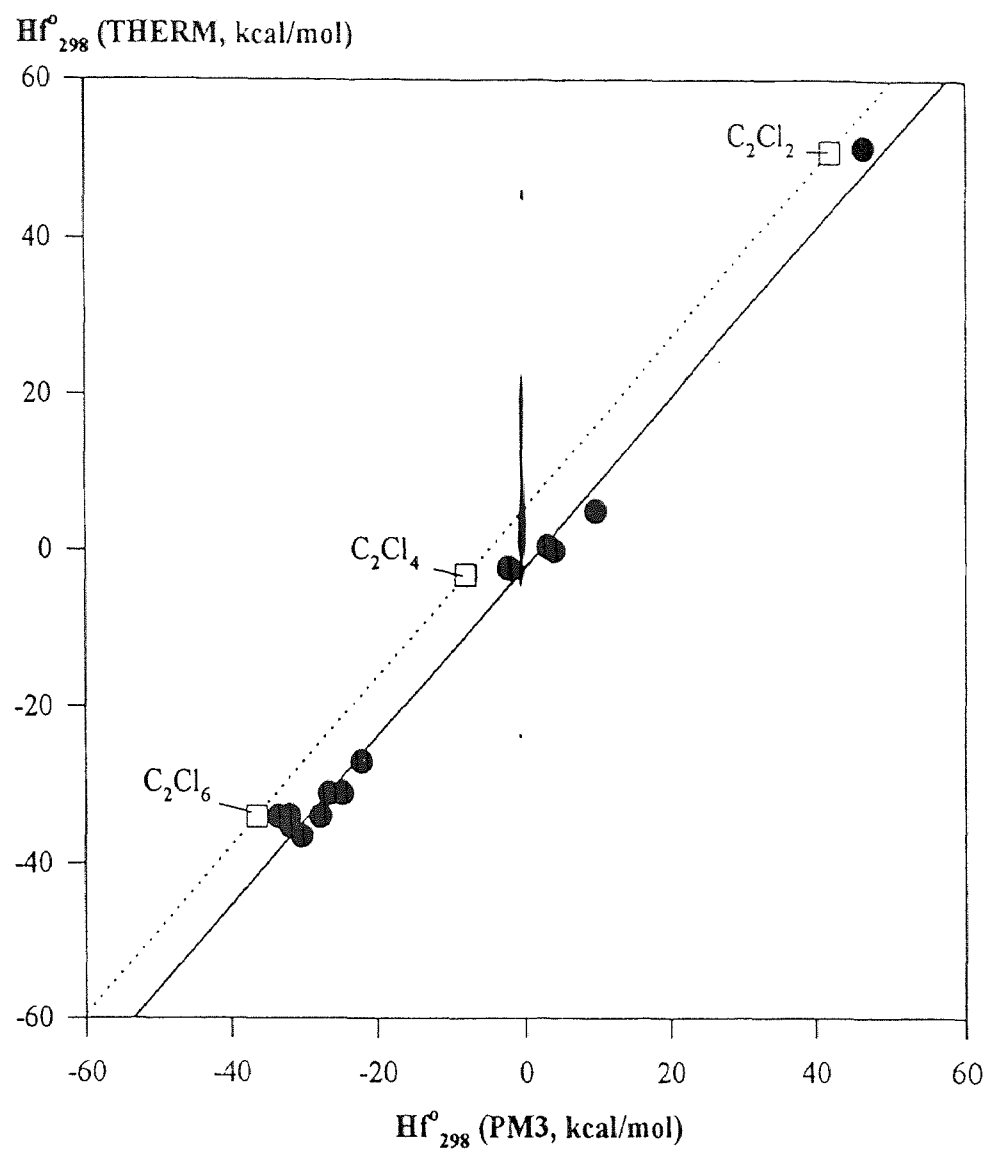
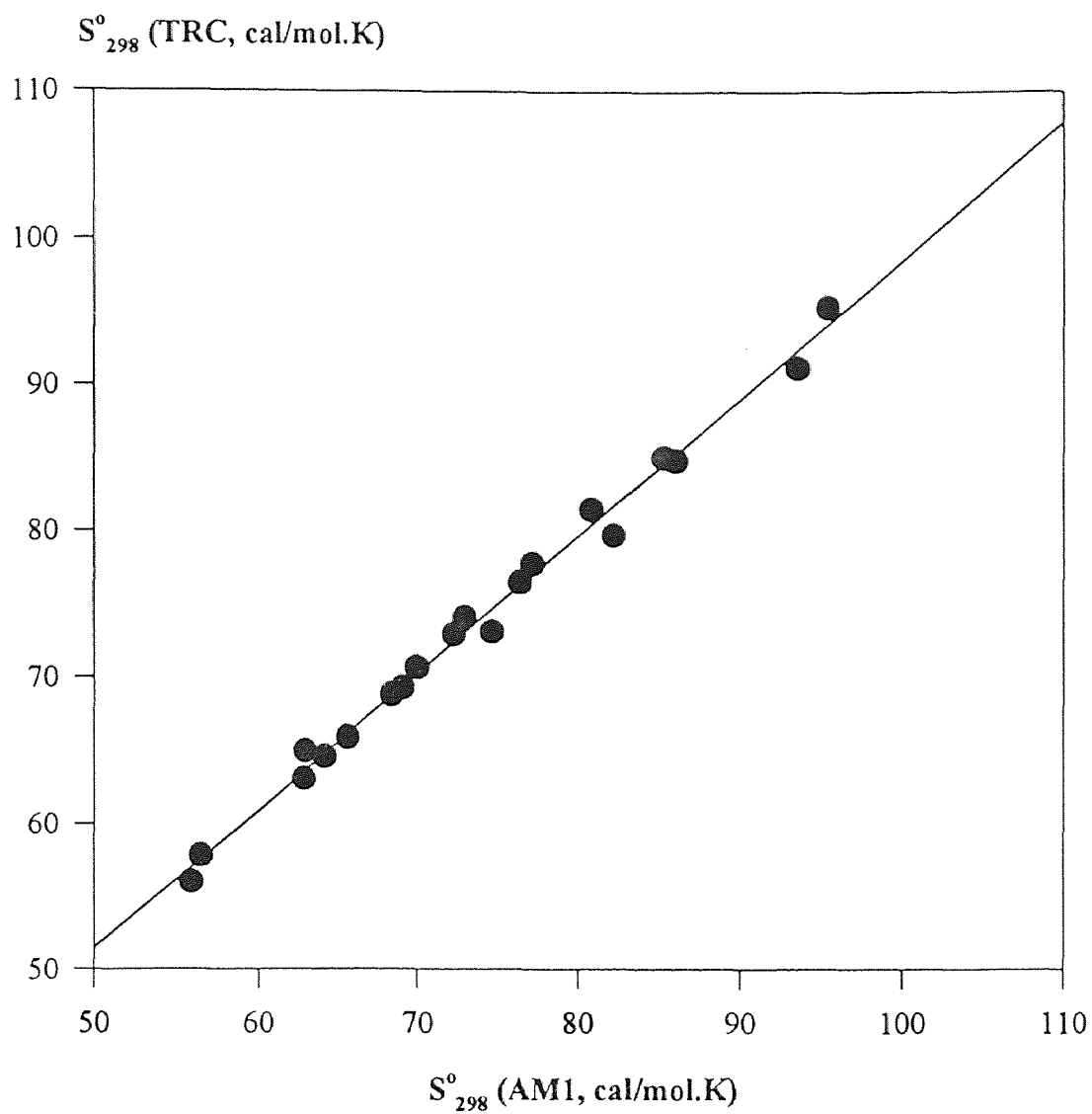


Figure IB. 6 Comparison of  $Hf_{298}^{\circ}$ : THERM vs. PM3



— All data:  $y = 0.94x + 4.41$ ,  $R^2 = 0.993$

$S^{\circ}_{298}$  of  $C_2HCl$  and  $C_2Cl_2$  are from JANAF (Ref. 2)  
since no TRC data are available

Figure IB. 7 Comparison of  $S^{\circ}_{298}$ : TRC vs. AM1

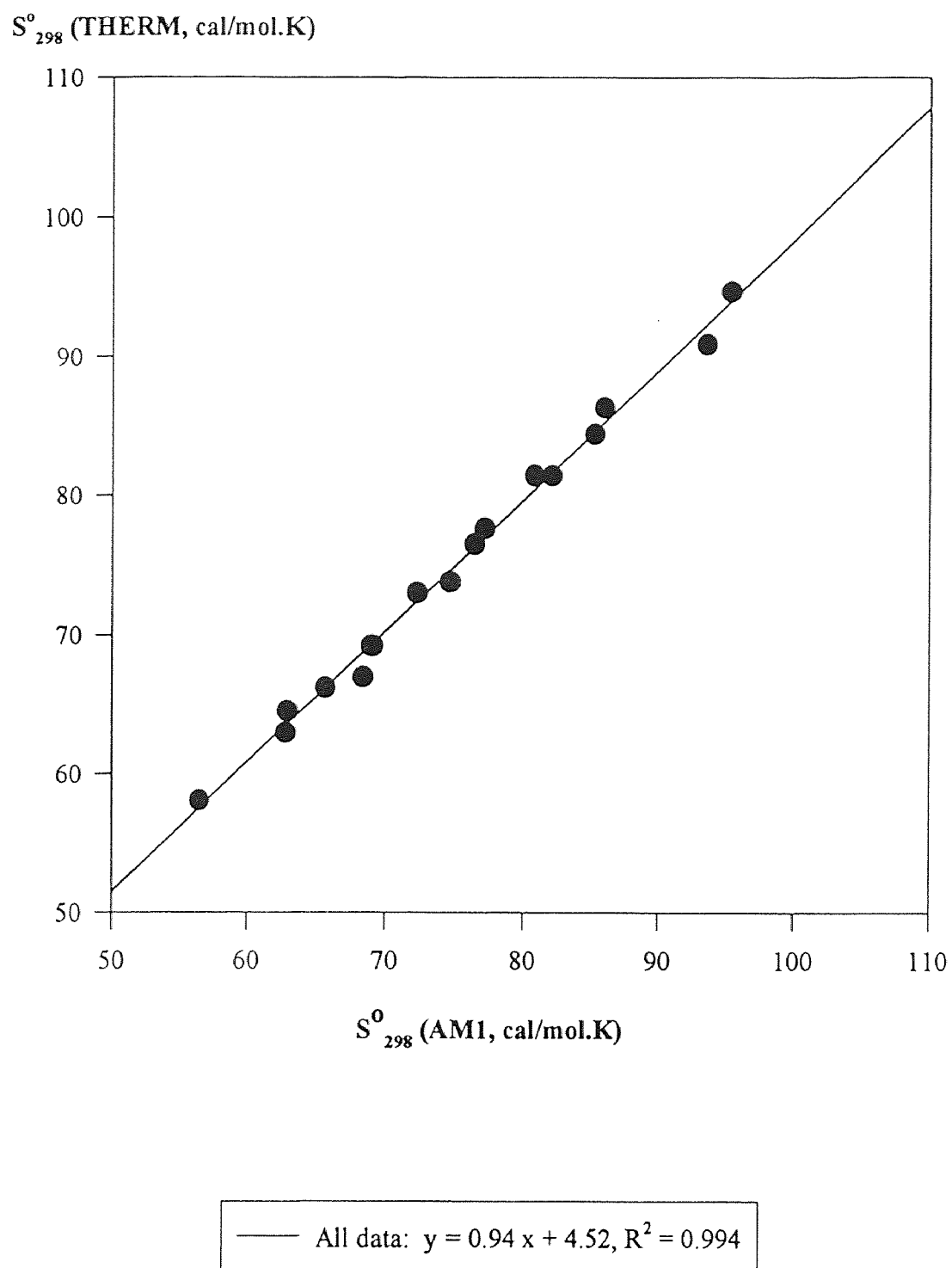
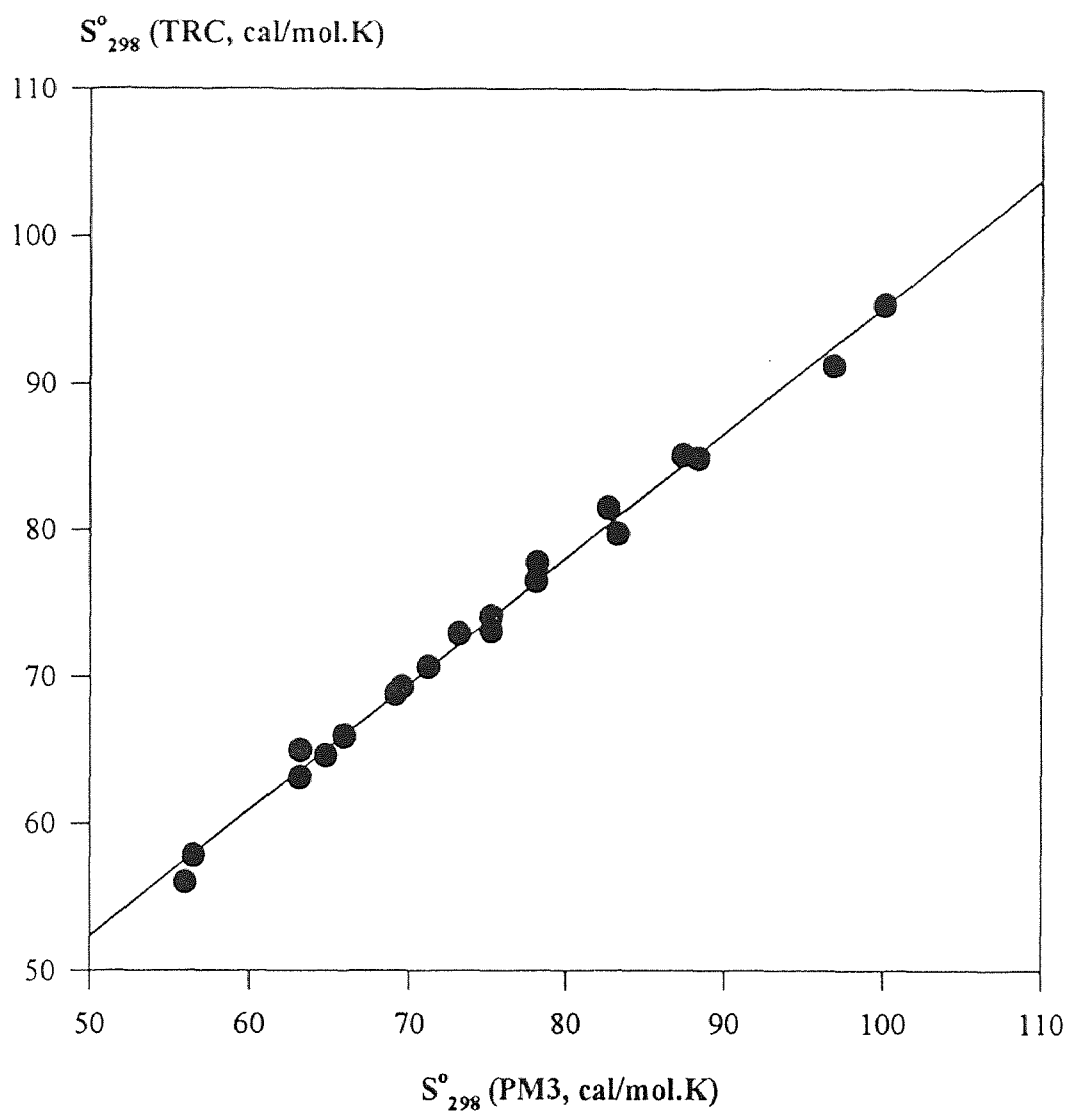


Figure IB. 8 Comparison of  $S^{\circ}_{298}$ : THERM vs. AM1



— All data:  $y = 0.86x + 9.46$ ,  $R^2 = 0.994$

$S^{\circ}_{298}$  of  $C_2HCl$  and  $C_2Cl_2$  are from JANAF (Ref. 2)  
since no TRC data are available

Figure IB. 9 Comparison of  $S^{\circ}_{298}$ : TRC vs. PM3

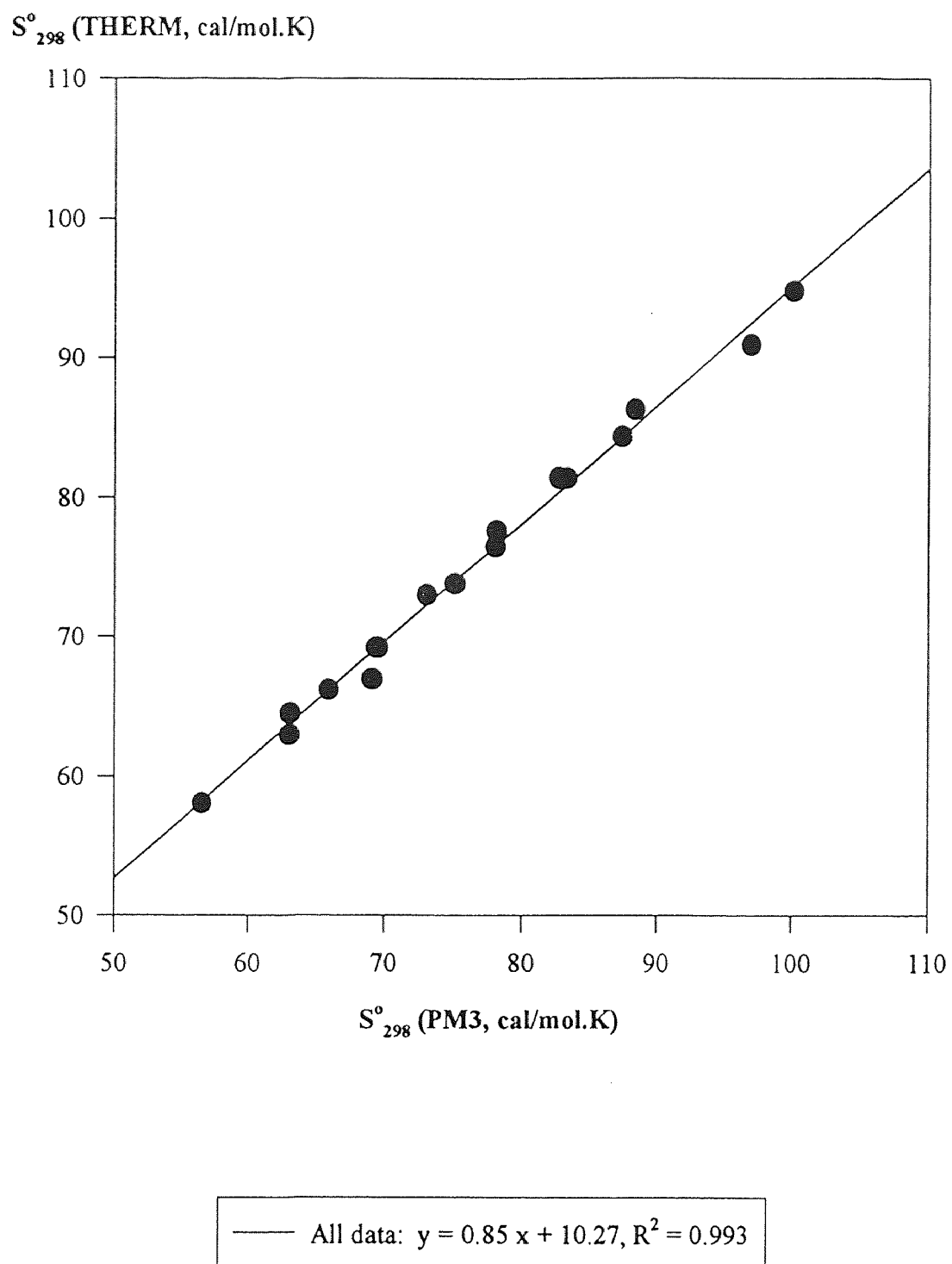


Figure IB. 10 Comparison of  $S^{\circ}_{298}$ : THERM vs. PM3

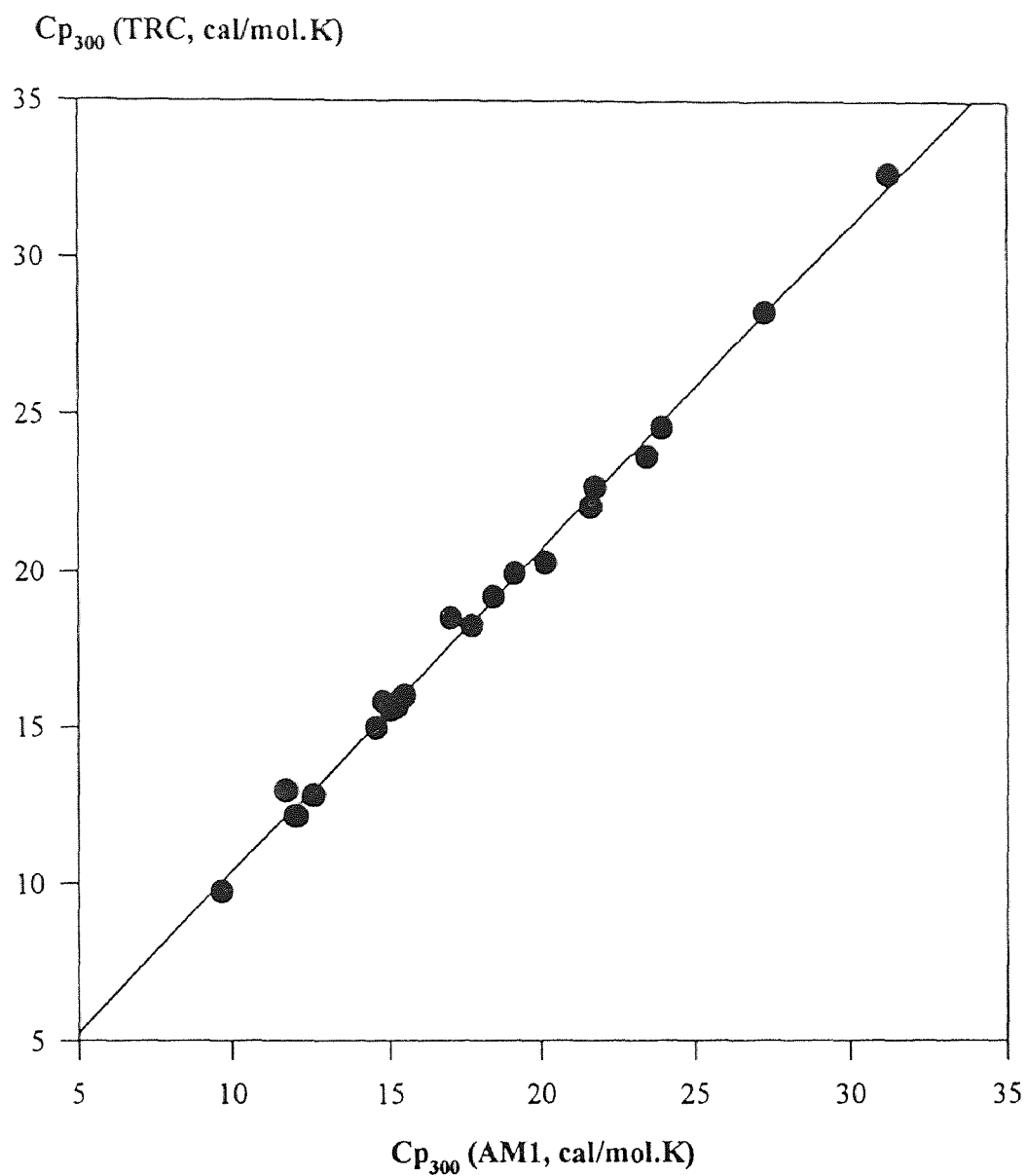


Figure IB. 11 Comparison of  $Cp_{300}$ : TRC vs. AM1



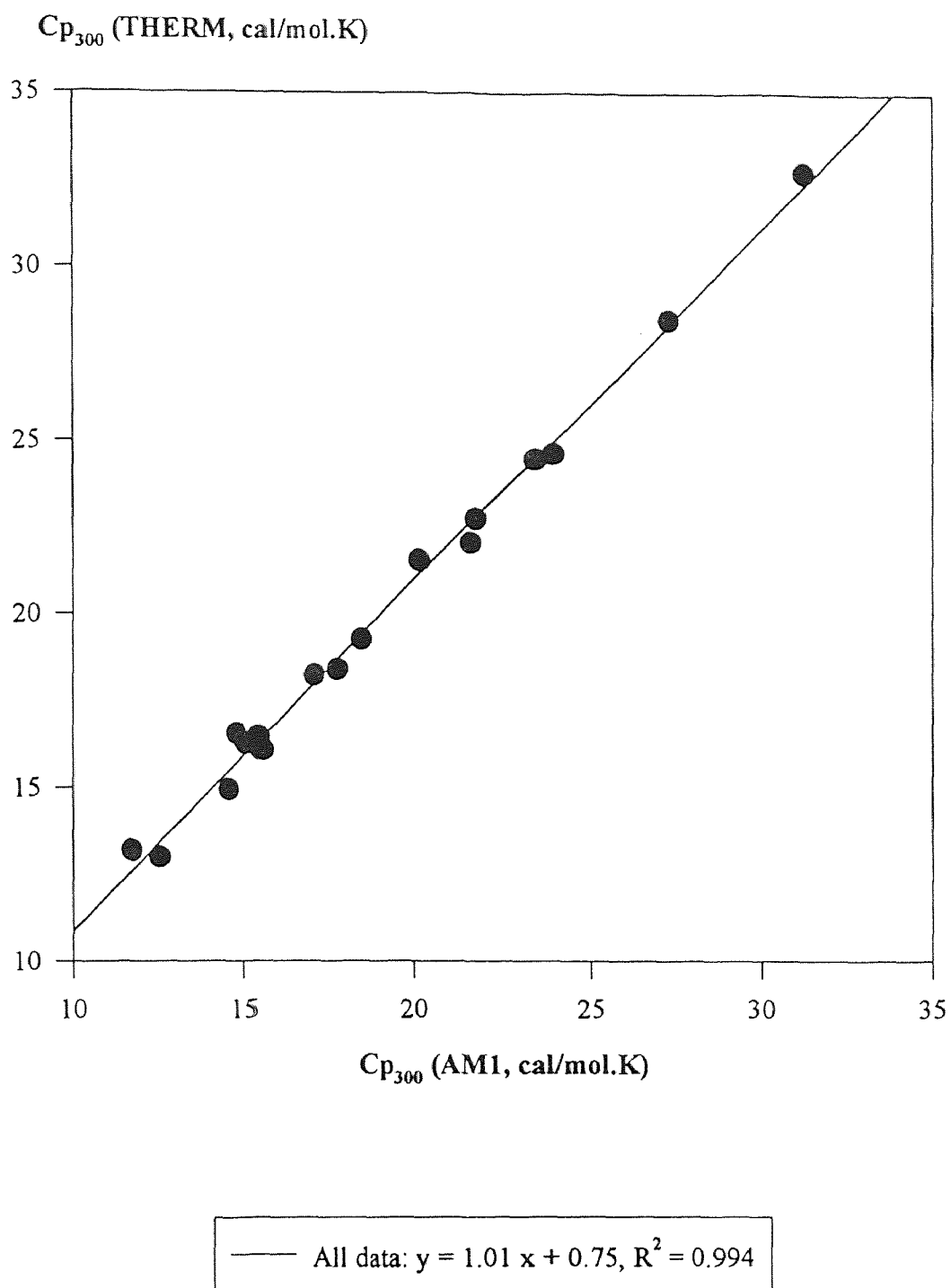
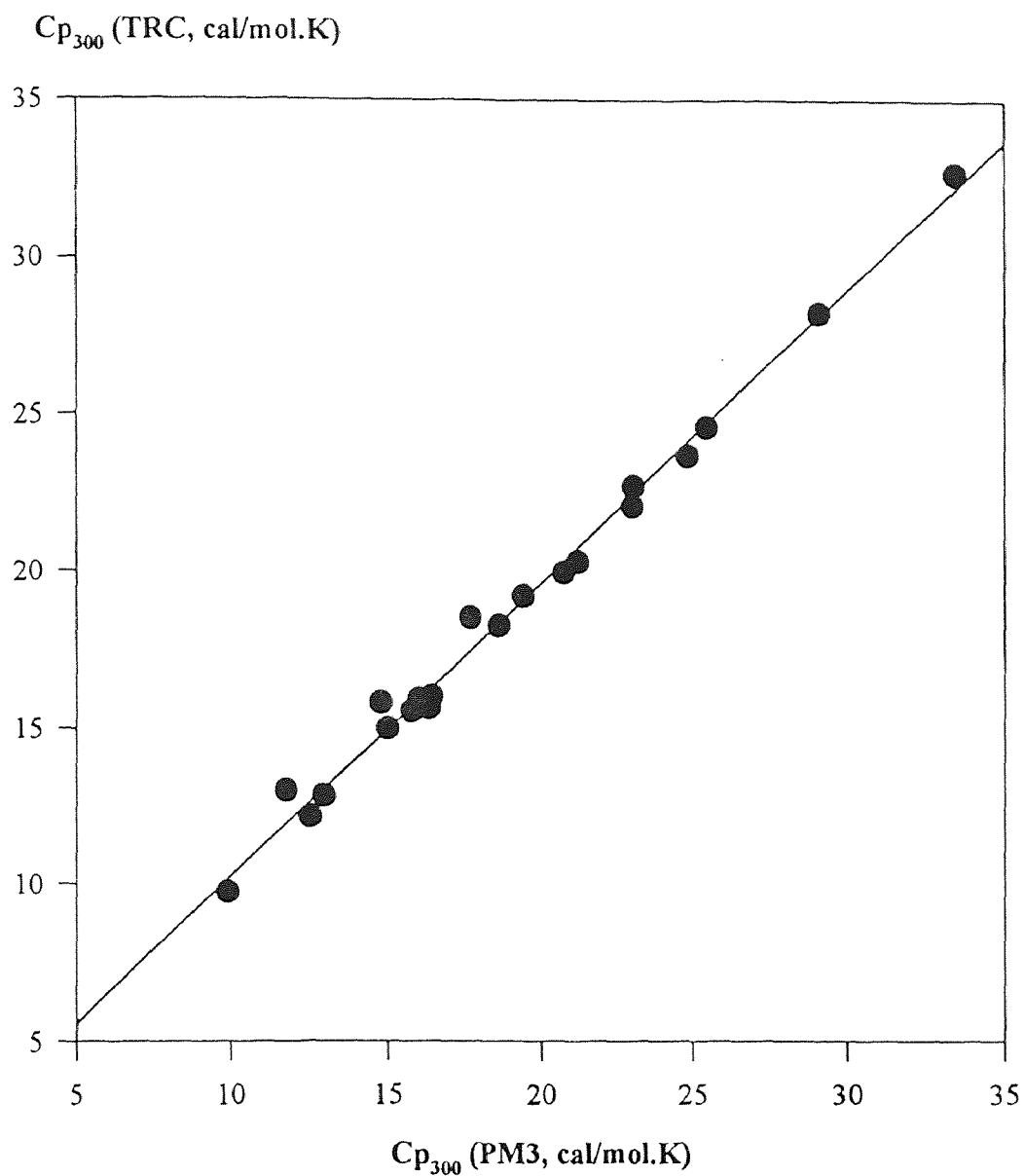


Figure IB. 12 Comparison of  $Cp_{300}$ : THERM vs. AM1



— All data:  $y = 0.94x + 0.89$ ,  $R^2 = 0.992$

$C_{p_{300}}$  of  $C_2HCl$  and  $C_2Cl_2$  are from JANAF (Ref. 2)  
since no TRC data are available

Figure IB. 13 Comparison of  $C_{p_{300}}$ : TRC vs. PM3

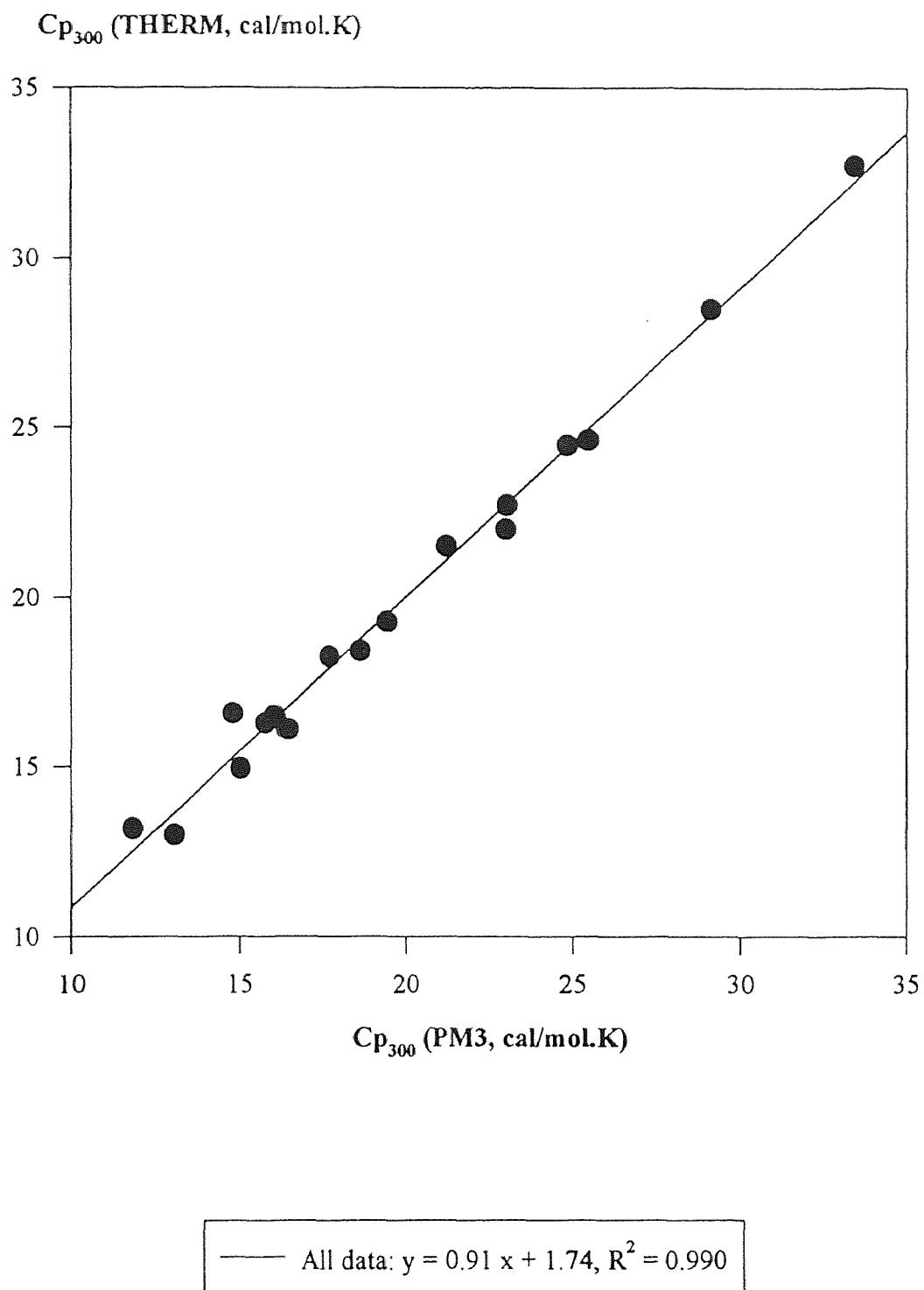


Figure IB. 14 Comparison of  $C_{p_{300}}$ : THERM vs. PM3

## CHAPTER 5

### SUMMARY

Thermodynamic properties,  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ ,  $C_p(T)$ , ( $300 \leq T/K \leq 1500$ ) for 21  $C_1$ ,  $C_2$  chlorocarbons are calculated by the AM1 and PM3 methods in MOPAC6, then compared with TRC literature<sup>1</sup> and modified group additivity values, where calculated values of  $S^\circ_{298}$ ,  $C_p(T)$  include substitution of contribution from a Pitzer and Gwinn<sup>35</sup> treatment of internal rotors in place of the MOPAC6 calculated torsion.

PM3-determined  $\Delta H_f^\circ_{298}$  have obvious differences from two references (Deviations from -8.08 to +7.12 kcal/mol). The calibrations between PM3-determined enthalpies and literature enthalpies are calculated as:  $\Delta H_f^\circ_{298, PM3} = -2.35 + 1.09 \times \Delta H_f^\circ_{298, literature}$  for hydrogen containing chlorocarbons;  $\Delta H_f^\circ_{298, PM3} = 5.36 + 1.07 \times \Delta H_f^\circ_{298, literature}$  for fully Cl substitute chlorocarbons;  $\Delta H_f^\circ_{298, PM3} = -2.19 + 1.08 \times \Delta H_f^\circ_{298, THERM}$  for hydrogen containing chlorocarbons;  $\Delta H_f^\circ_{298, PM3} = 5.48 + 1.08 \times \Delta H_f^\circ_{298, THERM}$  for fully Cl substitute chlorocarbons. AM1 is better than PM3 for prediction of standard enthalpies of formation of saturated  $C_1$ ,  $C_2$  chlorocarbons.

Standard entropies and heat capacities (300 to 1500K) calculated by AM1 or PM3 show good agreement with the references ( $R_d \leq \pm 5\%$ ). Only  $S^\circ_{298}$  of  $C_2HCl_3$  by PM3,  $C_p(300-500K)$  of  $C_2HCl$  and  $C_2Cl_2$  by AM1 and PM3 have more than  $\pm 5\%$  relative deviations.

Standard enthalpies of formation, entropies and heat capacities calculated by modified group additivity are in good agreement with TRC data: deviations of  $\Delta H_f^\circ_{298}$  are

less than 2 kcal/mol and relative deviations of  $S^{\circ}_{298}$  and  $C_p(T)$ , ( $300 \leq T/K \leq 1500$ ) are less than  $\pm 5\%$ .

AM1 and PM3 in MOPAC6 provide us accurate methods to estimate entropy and heat capacity for larger chlorocarbon species where limited or no experimental data are available. Enthalpy data from MOPAC6 AM1 and PM3 are not accurate enough for direct estimation. Density function or ab initio calculations at different levels can be tried but they are expensive and may not be able to deal very large molecules at present. Modified Group Additivity is recommended because it is faster, easier and more precise than semiempirical MOPAC6 calculations.

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## PART II

### REACTION OF OH RADICAL WITH $\text{C}_2\text{H}_3\text{Cl}$ , RATE CONSTANT AND REACTION PATHWAY ANALYSIS

## CHAPTER 1

### INTRODUCTION

Gas phase reactions of OH radicals are important in combustion and incineration of chlorinated hydrocarbon (CHCs) as well as in atmospheric chemistry. In combustion environments, OH is often the active radical present in the highest concentrations, where it serves to initiate breakdown of hydrocarbons (HCs) and it also reacts with CO producing CO<sub>2</sub>, plus H atoms, plus energy. Here if temperature is high, H atoms may react with O<sub>2</sub> in the critically important chain branching step  $H + O_2 \rightarrow OH + O$ . OH is often the most important active species in combustion and atmospheric oxidation process. It abstracts hydrogen atom from saturated hydrocarbons forming HC radicals, which then combine with O<sub>2</sub> forming peroxy radicals. Peroxy radical then reacts with NO or undergoes other reactions related to photochemical smog. OH radicals also add to unsaturated hydrocarbons and carbonyls forming radicals which then further react with O<sub>2</sub> and NO. Previous studies on OH radical reaction with unsaturated hydrocarbons such as vinyl chloride as well as this work show that the addition reaction is predominate at low temperature, while abstraction of H atom becomes important above 1400 K.

Howard<sup>1</sup> has determined the rate constant for reaction of OH with six different ethylene compounds (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>3</sub>Cl, C<sub>2</sub>HCl<sub>3</sub>, C<sub>2</sub>Cl<sub>4</sub>, CH<sub>2</sub>CF<sub>2</sub>, C<sub>2</sub>ClF<sub>3</sub>) at 296 K and in 0.7 - 7.0 torr helium buffer gas, using a discharge - flow reactor with Laser Magnetic Resonance (LMR) detection of OH. The rate constants at 7.0 torr are all in the range  $(1.2 - 4.2) \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , except for C<sub>2</sub>Cl<sub>4</sub> which is lower, about  $1.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The accuracy of the measurements was estimated to be about  $\pm 20\%$ . Howard measured 8 points between 0.7 and 7 torr. These data showed that the rate constant for OH reaction

with vinyl chloride to be pressure dependent (in the fall-off regime), increasing from  $1.2 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 0.7 torr to  $3.01 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at 7.0 torr, where it still was not at the high pressure limit.

Perry et al.<sup>2</sup> measured the absolute rate constants for reactions of OH radical with vinyl chloride, vinyl fluoride, and vinyl bromide by using a flash photolysis-resonance fluorescence technique over the temperature range 299-426 K at total pressure of ca. 50 torr (for  $\text{C}_2\text{H}_3\text{Cl}$  and  $\text{C}_2\text{H}_3\text{Br}$ ) or ca. 100 torr (for  $\text{C}_2\text{H}_3\text{F}$ ) of argon. They measured 6-8 points at each temperature for each reaction. The Arrhenius expressions for the rate constants (in  $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) obtained were:

$$k(\text{C}_2\text{H}_3\text{F} + \text{OH}) = 8.91 \times 10^{11} e^{(775 \pm 300)/RT} \text{ or } (3.35 \pm 0.34) \times 10^{12} \text{ at room temperature}$$

$$k(\text{C}_2\text{H}_3\text{Cl} + \text{OH}) = 6.87 \times 10^{11} e^{(1045 \pm 300)/RT} \text{ or } (3.97 \pm 0.40) \times 10^{12} \text{ at room temperature}$$

$$k(\text{C}_2\text{H}_3\text{Br} + \text{OH}) = 1.08 \times 10^{12} e^{(805 \pm 300)/RT} \text{ or } (4.10 \pm 0.42) \times 10^{12} \text{ at room temperature}$$

The k's decreased with the increasing temperature. Combining these data with the reference rate constant (note: high pressure) for OH + ethylene ( $4.73 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  which they measured before this work), they obtained the following relative rate constants:  $\text{C}_2\text{H}_4 : \text{C}_2\text{H}_3\text{Br} : \text{C}_2\text{H}_3\text{Cl} : \text{C}_2\text{H}_3\text{F} = 1 : 0.87 : 0.84 : 0.71$ . This appears to show a trend — the more electronegative the halogen substituent, the lower the rate constant. However, the total pressure from 100 to 52 torr for  $\text{C}_2\text{H}_3\text{F}$ , from 50 to 100 torr for  $\text{C}_2\text{H}_3\text{Cl}$  had no effect on the rate constants within the experimental errors ( $\pm 5\%$ ) at room temperature.

Liu et al.<sup>3</sup> studied the gas phase reaction of OH radical with vinyl chloride at 1 atm of argon over 313-1173K by using pulse radiolysis, resonant absorption for OH measurement. Temperature dependence of the rate constants showed behavior similar to that of OH + ethylene in that, the predominant reaction changed from an addition reaction below 588 K to abstraction of hydrogen atom above 723 K. They also observed negative temperature constant for the addition reaction as:  $1.29 \times 10^{12} e^{(700 \pm 120)/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The linear and nonlinear form rate constants for the H atom abstraction reaction were  $1.79 \times 10^{13} e^{(-4020 \pm 700)/RT}$  and  $8.43 \times 10^6 \times T^2 e^{(-1200)/RT} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . However, no measurement was made between 588 and 723K, and no reason was explained why there was such a big temperature jump in their experiment.

The low temperature addition reactions OH + C<sub>2</sub>H<sub>3</sub>Cl are complex and non-elementary. OH can add to either α- or β-carbon of C<sub>2</sub>H<sub>3</sub>Cl (α-carbon is the Cl-attached carbon, β-carbon is the carbon next to α-carbon). In each case, an adduct is formed, which can undergo stabilization via collisions, or before stabilization it may undergo unimolecular reaction to products, or reverse reaction — dissociation back to reactants. There are also two different C-H bond where abstraction can occur at the same time.

The summary of literature are shown in Table IIA. 1.

**Table IIA. 1** Previous studies on OH + C<sub>2</sub>H<sub>3</sub>Cl

Researchers	Experimental Technique	T (K)	P (torr)	k at room temp. (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	High Pressure Limit
Howard	Laser Magnetic Resonance	296	0.7-7.0	1.20e12 3.01e12	No
Perry et al.	Photolysis Resonance Fluorescence	299-426	50	3.97e12	Yes
Liu et al.	Pulse Radiolysis	313-1173	760	4.55e12	Yes

It would be helpful for both combustion and atmospheric kinetic modeling, to know the rate constants and specific reaction pathways for reaction of OH in each of the above four cases. A complete analysis of the OH addition reactions to the two carbon atom sites in vinyl chloride is presented in this work. The addition reactions are analyzed by multi-frequency Quantum RRK (Rice and Ramsperger and Kassel) analysis for  $k(E)$  and a modified strong collision approach of Gilbert et al.<sup>4</sup> The abstraction reactions have been analyzed by Ho et al. using Transition State Theory of Benson.<sup>5</sup> The rate constants are recommended for the two different addition reactions to specific products versus pressure. Thermodynamic parameters of the intermediate radicals and products are also listed.

## CHAPTER 2

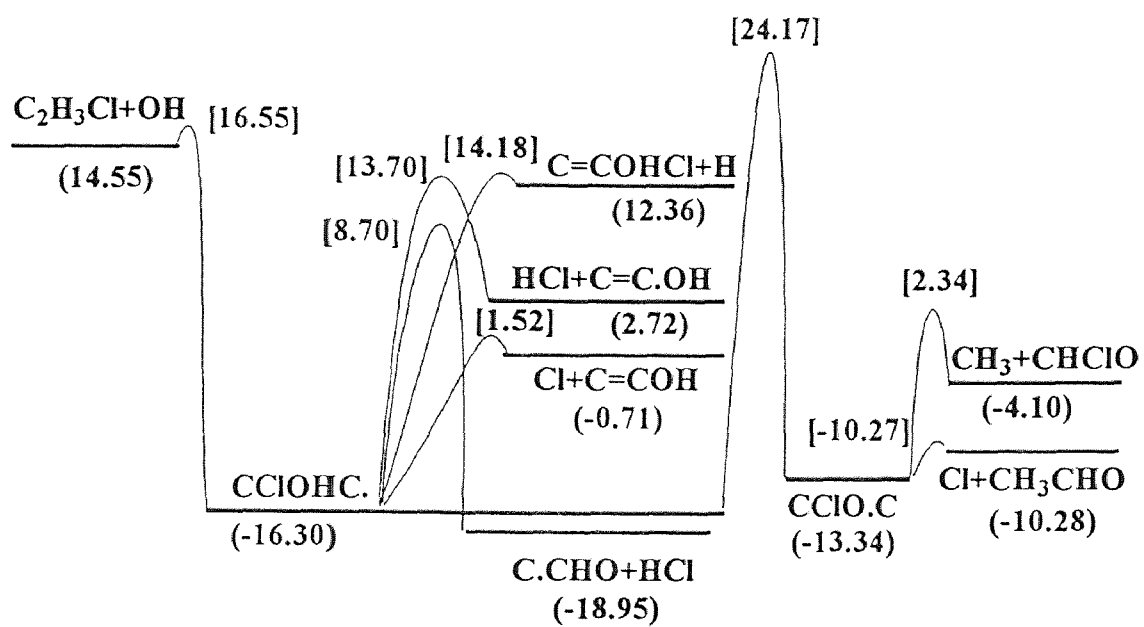
### THERMODYNAMIC PROPERTIES

#### 2.1 Thermodynamic Properties Stable Molecules and Their Daughter Radicals in $C_2H_3Cl + OH$ System

Thermodynamic properties including  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ ,  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) of reactants, intermediates and products were obtained from literature when available. Because thermodynamic properties for many chloro-oxy-carbon species have not been previously measured or calculated, we calculated their thermodynamic parameters using the techniques of Group Additivity<sup>5-6</sup> (see part I) and the "THERM"<sup>7-8</sup> (see part I) computer code. Bond dissociation energies from the literature<sup>9</sup> and hydrogen bond dissociation (BD) groups developed by Lay et al.<sup>10</sup> were used to calculate thermodynamic properties of the respective radicals and are listed in Table IIA. 2. The potential energy diagrams for the chemical reactions, both  $\alpha$ - and  $\beta$ -addition (to the  $C_D/Cl/H$  and  $C_D/H_2$  carbons respectively), is shown in Figures IIB. 1 and 2.

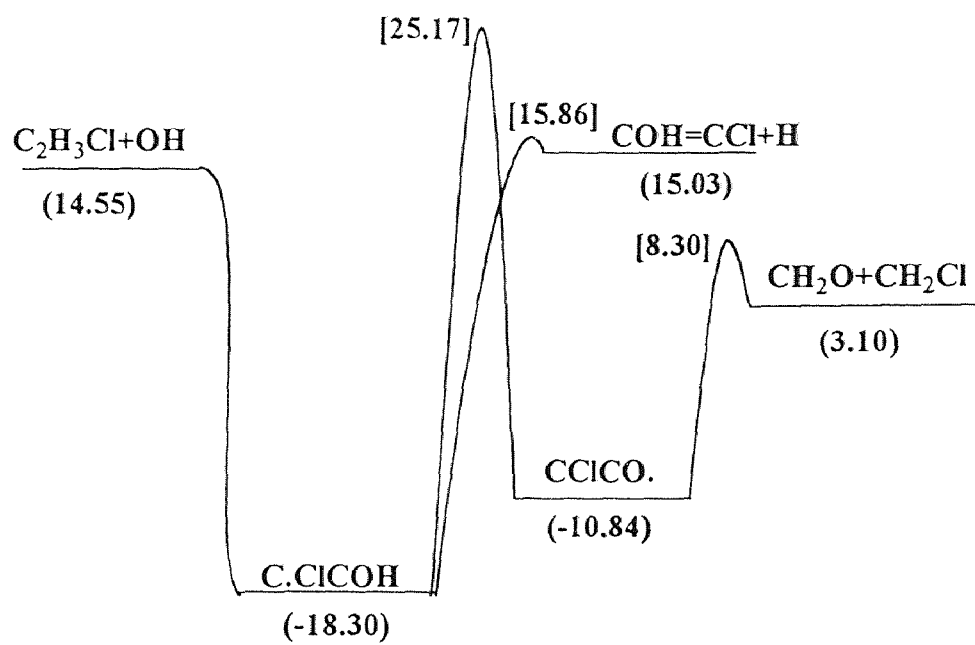
#### 2.2 Thermodynamic Properties of Molecules in Transition State

PM3 method in MOPAC6.0 was used to calculate the  $\Delta H_f^\circ_{298}$ ,  $S^\circ_{298}$ ,  $C_p(T)$  ( $300 \leq T/K \leq 1500$ ) of transition state structures of 12 elementary reactions in this  $C_2H_3Cl + OH$  system. The structures, moments of inertia and vibrational frequencies are listed in Figure IIB. 3 and Figure IIB. 4 for  $\alpha$ - and  $\beta$ -addition, respectively. The thermodynamic properties of these transition states are shown in Table IIA. 3.



unit: kcal/mol

Figure IIB. 1 Potential energy diagram for OH  $\alpha$ -addition to vinyl chloride



unit: kcal/mol

Figure IIB. 2 Potential energy diagram for OH  $\beta$ -addition to vinyl chloride



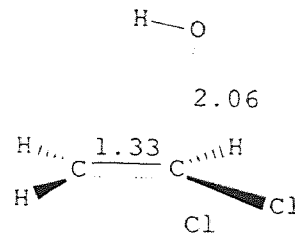
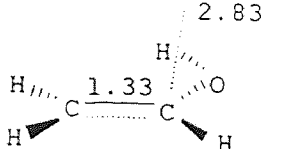
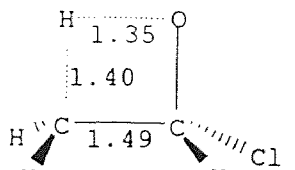
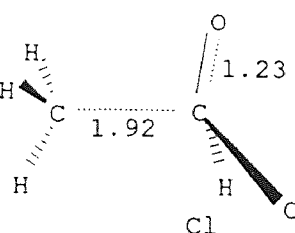
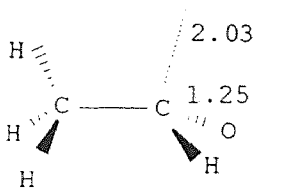
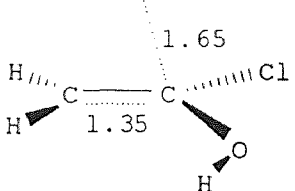
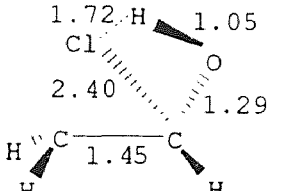
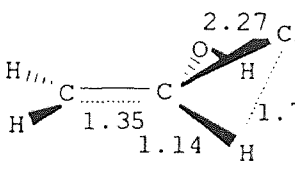
		Moments of Inertia (cm-1)	Vibrations (cm-1)		
	OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	0.290659	-479.11	642.69	1301.35
		0.126471	91.55	779.69	1711.00
		0.097523	149.21	990.09	2970.72
			292.94	1018.82	3314.75
			388.26	1101.92	3138.51
	CHClOHC.H <sub>2</sub> → Cl + C <sub>2</sub> H <sub>3</sub> OH	0.332346	-121.31	908.91	1419.88
		0.083322		949.76	1854.44
		0.068868	164.75	980.09	2997.91
			364.87	1073.48	3149.12
			512.14	1251.10	3164.85
	CHClOHC.H <sub>2</sub> → CHClO.CH <sub>3</sub>	0.397663	-2056.62	869.36	1249.87
		0.143764	316.83	973.62	1361.05
		0.117363	362.84	997.90	1625.70
			458.13	1018.94	2945.18
			618.31	1152.21	3117.64
	CHClO.CH <sub>3</sub> → CHClO + CH <sub>3</sub>	0.285734	-745.75	790.81	1323.00
		0.151170	83.09	813.16	1673.63
		0.108074	204.21	889.79	2901.69
			307.67	1076.65	3181.57
			421.05	1192.70	3197.75
	CHClO.CH <sub>3</sub> → Cl + CH <sub>3</sub> CHO	0.313893	-682.51	948.10	1396.08
		0.142887	-87.52	997.71	1639.71
		0.104931	208.89	1047.93	2703.40
			282.85	1104.23	3081.78
			475.81	1380.28	3089.64
	CHClOHC.H <sub>2</sub> → H + CH <sub>2</sub> CClOH	0.325987	-2335.18	656.90	1380.30
		0.168186	315.09	704.01	1406.97
		0.114867	345.68	954.08	1834.90
			408.68	977.10	3140.93
			486.64	1190.93	3150.04
	CHClOHC.H <sub>2</sub> → HCl + C.H <sub>2</sub> CHO	0.365028	-2108.42	786.77	1390.75
		0.138542	174.04	846.59	1466.11
		0.104150	271.85	897.35	1771.20
			415.12	993.34	2996.99
			609.32	1121.73	3118.16
	CHClOHC.H <sub>2</sub> → HCl + CH <sub>2</sub> C.OH	0.330556	-281.88	906.12	1355.47
		0.119376	123.10	945.15	1658.75
		0.091216	266.85	988.41	2543.24
			416.97	1056.70	3135.74
			476.69	1237.12	3152.03

Figure IIB. 3 Transition states of  $\alpha$ -addition of OH + C<sub>2</sub>H<sub>3</sub>Cl

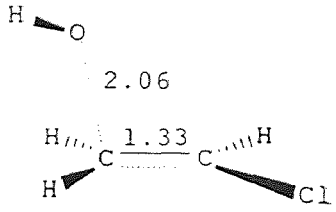
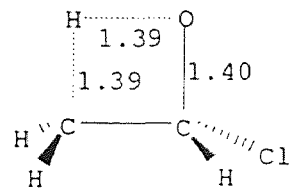
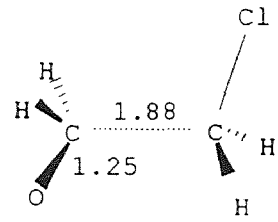
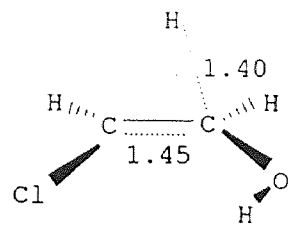
		Moments of Inertia (cm-1)	Vibrations (cm-1)		
	OH + C <sub>2</sub> H <sub>3</sub> Cl ->		-683.40	763.22	1287.98
	CH <sub>2</sub> OHC.HCl	0.613986	96.59	836.82	1685.69
		0.081257	142.42	942.29	3013.87
		0.078050	204.32	984.06	3062.64
			380.38	1166.30	3122.11
			637.42	1186.93	3987.21
	CH <sub>2</sub> OHC.HCl ->		-2593.51	899.48	1284.76
	CH <sub>2</sub> O.CH <sub>2</sub> Cl	0.623185	189.74	972.89	1401.54
		0.106441	343.97	1007.01	1622.08
		0.103612	581.84	1040.55	2976.61
			676.72	1153.28	3020.64
			819.00	1252.89	3057.36
	CHClO.CH <sub>3</sub> ->		-919.58	787.81	1320.51
	CH <sub>2</sub> O + CH <sub>2</sub> Cl	0.806519	74.15	1010.98	1638.75
		0.087250	236.68	1024.74	2945.85
		0.081317	281.18	1044.12	2981.17
			665.82	1144.08	3099.91
			682.84	1247.88	3101.18
	CH <sub>2</sub> OHC.HCl ->		-2656.19	862.26	1404.95
	H + CHClCHOH	1.091587	198.05	901.45	1535.53
		0.083878	283.64	1010.20	1989.17
		0.081109	329.18	1068.66	3030.43
			428.86	1170.51	3052.84
			753.06	1223.78	3879.94

Figure IIB. 4 Transition states of  $\beta$ -addition of OH + C<sub>2</sub>H<sub>3</sub>Cl

Table IIA. 2 Thermodynamic properties of all species in  $C_2H_3Cl + OH$  system<sup>a</sup>

Species <sup>b</sup>	$H_f^\circ_{298}$	$S^\circ_{298}$	Cp					
			300K	400K	500K	600K	800K	1000K
H	52.10	27.36	4.97	4.97	4.97	4.97	4.97	4.97
Cl	28.90	39.50	5.32	5.32	5.32	5.32	5.32	5.32
OH	9.49	43.88	6.95	6.99	7.04	7.08	7.20	7.34
HCl	-22.07	44.60	6.89	6.95	7.03	7.12	7.32	7.54
CH3	35.20	46.30	9.21	10.02	10.79	11.52	12.86	14.02
CH2O	-26.00	50.90	7.93	9.43	10.68	11.74	13.36	14.51
CH2Cl	29.10	58.51	9.97	11.42	12.60	13.55	14.94	15.88
CHClO	-39.30	61.81	11.11	12.41	13.48	14.36	15.68	16.61
C2H3Cl	5.06	63.01	13.00	15.56	17.81	19.70	22.37	24.37
CH2CHOH	-29.61	62.91	14.15	17.32	19.97	22.08	25.19	27.44
CH2C.OH	24.79	64.77	14.19	16.59	18.52	20.04	22.26	23.86
CH2COHCl	-39.74	71.71	17.40	19.26	20.83	22.73	25.29	27.28
CHOHCHCl	-37.07	70.70	16.95	20.16	22.76	24.78	27.42	29.27
CH3CHO	-39.18	63.13	13.22	15.71	18.22	20.47	24.22	26.97
C.H2CHO	3.12	60.40	12.92	15.31	17.44	19.24	22.10	24.12
CH2OHC.HCl	-18.30	78.91	18.61	21.60	24.30	26.17	29.48	31.88
CH2O.CH2Cl	-10.84	75.44	17.05	20.59	23.59	26.08	29.90	32.61
CHClOHC.H2	-16.30	77.26	17.30	19.67	22.05	24.21	27.77	30.26
CHClO.CH3	-13.34	72.40	16.41	19.18	21.92	24.37	28.27	30.98

a : Units:  $\Delta H_f^\circ_{298}$ , kcal/mol;  $S^\circ_{298}$  and Cp (T), cal/mol.K; b: · are radical sites.

Table IIA. 3 Thermodynamic properties of transition state in  $C_2H_3Cl+OH$  system

	$H_f^\circ_{298}$	$S^\circ_{298}$	Cp					
			300K	400K	500K	600K	800K	1000K
ts of reaction 1	26.88	75.48	18.11	21.28	23.84	25.88	28.95	31.22
ts of reaction 2	-16.54	72.78	16.90	20.06	22.74	24.94	28.27	30.74
ts of reaction 3	19.09	69.96	16.83	20.83	24.12	26.73	30.50	33.07
ts of reaction 4	2.85	74.86	17.54	20.73	23.36	25.50	28.78	31.21
ts of reaction 5	-6.15	72.69	17.51	20.70	23.41	25.63	29.02	31.50
ts of reaction 6	17.53	73.71	18.14	21.44	24.17	26.38	29.64	31.94
ts of reaction 7	7.84	73.34	15.82	19.16	22.07	24.50	28.27	31.02
ts of reaction 8	-4.12	74.05	17.31	20.45	23.08	25.24	28.57	31.02
ts of reaction 9	27.89	77.37	17.93	21.08	23.67	25.75	28.87	31.17
ts of reaction 10	22.92	70.34	16.28	20.27	23.63	26.33	30.25	32.93
ts of reaction 11	7.93	77.57	16.51	19.88	22.74	25.06	28.58	31.16
ts of reaction 12	5.40	73.73	17.39	20.56	23.35	25.66	29.13	31.60

Units:  $\Delta H_f^\circ_{298}$ , kcal/mol;  $S^\circ_{298}$  and Cp (T), cal/mol.K

## CHAPTER 3

### QRRK CALCULATIONS FOR ADDITION REACTIONS OF $C_2H_3Cl + OH$

A method to treat chemical activation reaction systems, which provides a framework to evaluate product channel distributions and fall-off effects as they change with temperature and pressure was developed by Dean<sup>11</sup>. This approach is based on the quantum version of Kassel theory (QRRK)<sup>12</sup> to estimate the  $k(E)$ 's (dissociation rates of the energized adduct). The current version of the computer code utilizes a reduced set of vibration frequencies which accurately reproduce the molecule (adduct) heat capacity data, plus one external rotation in order to calculate density of states  $\rho(E)$ . Comparisons of ratios of these  $\rho(E)/Q$  (partition function  $Q$ ) with direct count  $\rho(E)/Q$  are shown to be in good agreement.<sup>13</sup> Non-linear Arrhenius effects resulting from changes in the thermodynamic properties of the respective transition states relative to the adduct with temperature are incorporated using a two-parameter Arrhenius pre-exponential factor ( $A, n$ ) in  $AT^n$ . Fall-off is incorporated using modified strong collision approach (beta collision) of Gilbert et al.<sup>4</sup>. Comparisons of calculation for this  $OH + C_2H_3Cl$  system with ones using a Master Equation formalism<sup>14</sup> yield results which are effectively identical to ones presented in this study.

Branching ratios for vinyl chloride +  $OH$  reactions at different temperature and pressure were calculated using this procedure. Pre-exponential  $A$  factors and activation energies ( $E_a$ ) for the bimolecular addition/combination and the isomerization reactions at the high pressure limit were obtained from literature<sup>15</sup>, Transition State Theory and thermochemical kinetic methods of Benson<sup>16</sup>.  $A$  and  $E_a$  for the dissociation reactions, back to reactants, and to products come from analysis of thermodynamic heats of

formation, entropies for the relevant species and were obtained from the reversal addition or combination reaction rate constants by applying the Microscopic Reversibility (MR):

$$k_{eq.} = k_f / k_r.$$

Where  $k_{eq.}$  — equilibrium constant;

$k_f$  — rate constant of forward reaction;

$k_r$  — rate constant of reverse reaction.

Details on specific reaction rates are described in the following chapters.

## CHAPTER 4

### ADDITION AND ABSTRACT REACTIONS OF $C_2H_3Cl + OH$

The input parameters, high pressure limit rate constants, and the sources are listed in Tables IIA. 4 and IIA. 5 for OH addition to the  $\alpha$ - and  $\beta$ -carbon sites in  $CH_2=CHCl$  respectively. The parameters in Tables IIA. 4 and IIA. 5 are referenced to the ground (stabilized) state of the complex because this is the formalism used in QRRK Theory.

#### 4.1 $\alpha$ -Addition of $OH + C_2H_3Cl$ and the Continuing Reactions

Two parameter Arrhenius pre-exponential factors  $A_1$ ,  $n_1$  are calculated from Transition State Theory (TST).

$$A' = A \times T^n = e^m \times (k_B T/h) \times (P^0/RT)^{1-m} \times e^{\Delta S^\ddagger,0/R}$$

$$E_a = \Delta H^\ddagger,0 + mRT$$

Where  $k_B$  — Boltzman constant

$h$  — Planck constant;

$R$  — The ideal gas constant;

$m$  — 1 (unimolecular reaction) or 2 (bimolecular reaction).

Two parameters ( $A_1$ ,  $n_1$ ) of the high pressure limit rate constant for OH addition to the  $\alpha$ -carbon ( $k_1$  in Table IIA. 4) are obtained by applying bimolecular TST. Since OH addition to  $\alpha$ -carbon is more hindered by the chlorine atom than that to  $\beta$ -carbon,  $E_a$  for  $\alpha$ -addition ( $E_{a1}$ ) should be higher than that for  $\beta$ -addition. Here  $E_{a1}$  is assigned as 2 kcal/mol. The reverse reaction  $k_{-1}$  is calculated from  $k_1$  by the Microscopic Reversibility (MR).

The isomerization reaction  $k_3$  is obtained from unimolecular transition state. Activation energy of this isomerization  $E_{a3}$  is estimated from the transition state structure which is 1,2-hydrogen shift via four-member ring. So  $E_{a3} = \text{energy of ring strain} + E_{abs} + \Delta H_{rxn} = 40.47 \text{ kcal/mol}$ , where the ring strain for four member ring is 26 kcal/mol, abstraction energy of H atom by a primary carbon site,  $E_{abs}$ , is 11.51 kcal/mol, and  $\Delta H_{rxn}$  of this isomerization is 2.96 kcal/mol.

Rate constants for dissociation to products  $k_2$ ,  $k_4$ ,  $k_5$ ,  $k_6$ ,  $k_7$  and  $k_8$ , are obtained from application of thermodynamics and the microscopic reversibility (MR) to the respective reverse addition reactions. The input parameters and literature references for all reactions in the  $\alpha$ -addition systems are listed in Table IIA. 4.

OH addition to the  $\alpha$ -carbon forms the  $\text{CHClOHC.H}_2^\#$  energized adduct. There is an obvious presence of a low energy channel for the this adduct: Cl atom elimination ( $k_2$ ):



This makes vinyl alcohol the dominate product of this adduct's formation for all conditions (temperature and pressure). Unimolecular isomerization ( $k_3$ ) of this adduct requires higher energy than that of the initial reactants at atmospheric conditions, so only a relative small fraction will isomerize, and further react at high temperature due to the higher  $E_a$  and the tight transition state.

Lennard-Jones parameters in Table IIA. 4 and Table IIA. 5 were obtained from tabulations<sup>17</sup> and a calculation method based on molar volumes and compressibility<sup>18</sup>.

Table IIA. 4 Input parameters of  $\alpha$ -addition of  $C_2H_3Cl + OH$  for the quantum Kassel calculation

Reaction	<sup>3</sup> A(cm <sup>3</sup> , mol, sec)	n	Ea(kcal/mol)
k <sub>1</sub> C <sub>2</sub> H <sub>3</sub> Cl + OH → CHClOHC.H <sub>2</sub>	2.7812E+7	1.71980	2
k <sub>-1</sub> CHClOHC.H <sub>2</sub> → C <sub>2</sub> H <sub>3</sub> Cl + OH	9.8764E+7	1.71980	32.09
k <sub>2</sub> CHClOHC.H <sub>2</sub> → Cl + CH <sub>2</sub> CHOH	7.4183E+11	1.4122	17.82
k <sub>3</sub> CHClOHC.H <sub>2</sub> → CHClO.CH <sub>3</sub>	8.2793E+8	1.04958	40.47
k <sub>-3</sub> CHClO.CH <sub>3</sub> → CHClOHC.H <sub>2</sub>	1.6635E+10	1.04958	37.23
k <sub>4</sub> CHClO.CH <sub>3</sub> → CHClO + CH <sub>3</sub>	2.2344E+13	0.30289	15.68
k <sub>5</sub> CHClO.CH <sub>3</sub> → Cl + CH <sub>3</sub> CHO	4.3012E+12	0.39427	3.07
k <sub>6</sub> CHClOHC.H <sub>2</sub> → H + CH <sub>2</sub> CClOH	1.1168E+10	0.95470	30.48
k <sub>7</sub> CHClOHC.H <sub>2</sub> → HCl + C.H <sub>2</sub> CHO	9.2185E+11	0.12430	25
k <sub>8</sub> CHClOHC.H <sub>2</sub> → HCl + CH <sub>2</sub> C.OH	4.1391E+11	0.35209	30

- k<sub>1</sub> A<sub>1</sub> from TST. Ea<sub>1</sub> = 2, evaluated for OH addition to CH<sub>2</sub>=CHCl  
k<sub>-1</sub> Thermodynamics and microscopic reversibility <MR>  
k<sub>2</sub> A<sub>2</sub> from TST. Ea<sub>2</sub> from Ea<sub>-2</sub>, Ea<sub>-2</sub> = 2.5, evaluated for Cl addition to CH<sub>2</sub>=CHOH  
k<sub>3</sub> A<sub>3</sub> from TST, Ea<sub>3</sub> = ring strain + E<sub>abs</sub> + ΔH = 26 + 11.5 + 2.96 = 40.47  
k<sub>-3</sub> <MR>  
k<sub>4</sub> A<sub>4</sub> from TST. Ea<sub>4</sub> from Ea<sub>-4</sub>, Ea<sub>-4</sub> = 8.0 from 0.5 for CH<sub>3</sub> + C<sub>2</sub>H<sub>4</sub> (ref. 57)  
k<sub>5</sub> A<sub>5</sub> from TST. Ea<sub>5</sub> from Ea<sub>-5</sub>, Ea<sub>-5</sub> = 1.0, evaluated for Cl addition to CH<sub>3</sub>CHO  
k<sub>6</sub> A<sub>6</sub> from TST. Ea<sub>6</sub> from Ea<sub>-6</sub>. Ea<sub>-6</sub> = 2.1 from k<sub>-6</sub> ≅ 10<sup>11.1</sup> for H + CH<sub>2</sub>=C(CH<sub>3</sub>)<sub>2</sub>. (ref. 57)  
k<sub>7</sub> A<sub>7</sub> from TST, Ea<sub>7</sub> = 25, evaluated for HCl elimination via 4-member-ring  
k<sub>8</sub> A<sub>8</sub> from TST, Ea<sub>8</sub> = 30, evaluated for HCl elimination via 3-member-ring

-----  
Reduced frequency sets for CHClOHC.H<sub>2</sub> (from CPFIT<sup>12</sup>)

VIBRATION #1: MODES = 5.510 FREQUENCY = 344.8 cm<sup>-1</sup>

VIBRATION #2: MODES = 8.127 FREQUENCY = 1517.9 cm<sup>-1</sup>

VIBRATION #3: MODES = 3.363 FREQUENCY = 3999.7 cm<sup>-1</sup>

GEO MEAN VIBRATION: MODES = 17.000, FREQUENCY = 1137.3 cm<sup>-1</sup>

Reduced frequency sets for CHClO.CH<sub>3</sub> (from CPFIT<sup>12</sup>)

VIBRATION #1: MODES = 5.447 FREQUENCY = 419.1 cm<sup>-1</sup>

VIBRATION #2: MODES = 8.911 FREQUENCY = 1522.3 cm<sup>-1</sup>

VIBRATION #3: MODES = 3.141 FREQUENCY = 3999.9 cm<sup>-1</sup>

GEO MEAN VIBRATION: MODES = 17.500, FREQUENCY = 1211.8 cm<sup>-1</sup>

Lennard-Jones parameters: σ = 4.55 Å, ε/k = 576.7 K



## 4.2 $\beta$ -Addition of OH + C<sub>2</sub>H<sub>3</sub>Cl and the Continuing Reactions

The parameters of rate constant for OH addition at the  $\beta$ -carbon of C<sub>2</sub>H<sub>3</sub>Cl ( $A_9$  and  $E_{a9}$  in Table IIA. 5) are  $1.29 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $-0.7 \text{ kcal/mol}$  which are abstracted from Liu et al.<sup>3</sup>. The reverse reaction  $k_{-9}$  is calculated from MR.

$A_9$ , and  $n_9$  calculated from bimolecular TST are also shown in the bottom of Table IIA. 5. The reason for not using them in QRRK calculation will be discussed in Chapter 5.

The unimolecular isomerization reaction  $k_{10}$  is obtained from TST and  $E_{a10}$  = energy of ring strain +  $E_{\text{abs}}$  +  $\Delta H_{\text{rxn}}$  =  $26 + 10.01 + 7.46 = 43.47 \text{ kcal/mol}$ . Dissociation reactions  $k_{11}$ ,  $k_{12}$  to products CH<sub>2</sub>O + CH<sub>2</sub>Cl and H + CHCl=CHOH are obtained from the reverse combination reactions and MR. The input parameters and literature references for all reactions in the  $\beta$ -addition systems are listed in Table IIA. 5.

The OH addition reaction to the  $\beta$ -carbon forms the CH<sub>2</sub>OHCHCl<sup>#</sup> energized adduct. Unimolecular isomerization ( $k_{10}$ ) of this adduct requires higher energy than that of the initial reactants when ring strain +  $E_a$  of H abstraction +  $\Delta H_{\text{rxn}}$  are considered. Relative small fractions of this adduct will isomerize and further react at higher temperatures due to high barrier and the tight TST. The adduct is, therefore, either stabilized or it dissociates back to the initial reactants (C<sub>2</sub>H<sub>3</sub>Cl + OH), as this is the lowest energy dissociation channel.

Table II.A. 5 Input parameters of  $\beta$ -addition of  $C_2H_3Cl + OH$  for the quantum Kassel calculation

Reaction	$A(\text{cm}^3, \text{mol}, \text{sec})$	n	$E_a(\text{kcal/mol})$
$k_9^a$ $C_2H_3Cl + OH \rightarrow CH_2OHC.HCl$	$1.29E+12$	0	-0.7
$k_{-9}^b$ $CH_2OHC.HCl \rightarrow C_2H_3Cl + OH$	$1.37E+12$	0	29.39
$k_{10}$ $CH_2OHC.HCl \rightarrow CH_2O.CH_2Cl$	$8.5120E+7$	1.23115	43.47
$k_{-10}$ $CH_2O.CH_2Cl \rightarrow CH_2OHC.HCl$	$1.0384E+9$	1.23115	35.85
$k_{11}$ $CH_2O.CH_2Cl \rightarrow CH_2O + CH_2Cl$	$1.5579E+14$	-0.07821	19.14
$k_{12}$ $CH_2OHC.HCl \rightarrow H + \dot{C}HCl=CHOH$	$3.3427E+9$	0.91969	34.61

$k_9$   $A_9$  from TST,  $E_{a9} = -0.7^3$

$k_{-9}$  <MR>

$k_{10}$   $A_{10}$  from TST,  $E_{a10} = \text{ring strain} + E_{ab} + \Delta H = 26 + 10.01 + 7.46 = 43.47$

$k_{-10}$  <MR>

$k_{11}$   $A_{11}$  from TST,  $E_{a11}$  from  $E_{a11}$ .  $E_{a11} = 8.0$  from  $C_2H_5 + C_2H_4$  (ref. 57)

$k_{12}$   $A_{12}$  from TST,  $E_{a12} = 1.5$ , evaluated for H addition to  $\dot{C}HOH=CHCl$

Reduced frequency sets for  $CH_2OHC.HCl$  (from CPFIT<sup>12</sup>)

VIBRATION #1: MODES = 4.652 FREQUENCY =  $250.5 \text{ cm}^{-1}$

VIBRATION #2: MODES = 7.603 FREQUENCY =  $1062.2 \text{ cm}^{-1}$

VIBRATION #3: MODES = 4.745 FREQUENCY =  $3022.4 \text{ cm}^{-1}$

GEO MEAN VIBRATION: MODES = 17.000, FREQUENCY =  $957.9 \text{ cm}^{-1}$

Reduced frequency sets for  $CH_2O.CH_2Cl$  (from CPFIT<sup>12</sup>)

VIBRATION #1: MODES = 6.761 FREQUENCY =  $519.0 \text{ cm}^{-1}$

VIBRATION #2: MODES = 7.207 FREQUENCY =  $1380.4 \text{ cm}^{-1}$

VIBRATION #3: MODES = 3.532 FREQUENCY =  $3234.8 \text{ cm}^{-1}$

GEO MEAN VIBRATION: MODES = 17.500, FREQUENCY =  $1123.4 \text{ cm}^{-1}$

a:  $k_9$  calculated by TST:  $A_9 = 9.0747E+7$ ,  $n_9 = 1.67739$

b:  $k_{-9}$  calculated by TST: <MR>  $A_{-9} = 9.6611E+7$ ,  $n_{-9} = 1.67739$

### 4.3 Transition-State-Theory Calculations for Abstraction Reactions of $\text{C}_2\text{H}_3\text{Cl} + \text{OH}$

This part of work was done by Winpin Ho and Joseph. W. Bozzelli. Their methods and results are summarized as following:

The pre-exponential A factors for bimolecular abstraction reactions were calculated using TST of Cohen and coworkers<sup>19-22</sup>. Modified Evans-Polanyi plot was used for obtaining the activation energy. The rate constants for these two abstraction channels are:

$$k_a = 1.40 \times 10^7 \times T^2 e^{-5310/RT} \text{ in cm}^3, \text{ mol, sec}$$

$$k_b = 2.54 \times 10^7 \times T^2 e^{-6200/RT} \text{ in cm}^3, \text{ mol, sec}$$

where  $k_a$ , is the rate constants for  $\alpha$ -abstraction channel:  $\text{OH} + \text{CH}_2=\text{CHCl} \rightarrow \text{CH}_2=\text{C}.\text{Cl} + \text{H}_2\text{O}$ ; and  $k_b$  for  $\beta$ -abstraction channel:  $\text{OH} + \text{CH}_2=\text{CHCl} \rightarrow \text{C}.\text{H}=\text{CHCl} + \text{H}_2\text{O}$ , respectively.

Above  $k_a$  and  $k_b$  are assumed to be pressure independent.

## CHAPTER 5

### RESULTS AND DISCUSSIONS

#### 5.1 RESULTS

Howard<sup>1</sup> has predicted that elimination of Cl from the adduct with formation of vinyl alcohol ( $k_2$  in this work) dominates for the  $\alpha$ -addition. Perry et al.<sup>2</sup> estimated the rate constant of this channel is about  $6.0 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  at room temperature which is about 15% of total rate constant. Our calculation shows that OH addition to the  $C_D/Cl/H$  carbon is a low fraction of that for addition to the  $C_D/H_2$  carbon; 10-20%, which is in agreement with the estimation of Perry et al.<sup>2</sup> This channel behaves differently than  $\beta$ -addition due to the lower energy (exothermic relative to the initial reactants) reaction channel available to the adduct — unimolecular elimination of Cl. This product slate dominates for the  $\alpha$ -addition channel at all pressures and all temperatures (0.076 to 7600 torr, 300 to 1500K).

Figure IIB. 5 presents a plot of rate constants versus  $1000/T$  for the various channels resulting from OH addition at the  $\alpha$ -carbon at 760 torr. The apparent rate parameters to the specific product channels are listed in Table IIA. 6. The vinyl alcohol + Cl channel dominates the reaction in the temperature range 300-1500K. As temperature increases, other product channels (excluding stabilization) start to become more important; but are still below the major product channel — vinyl alcohol + Cl at 1500K. The stabilization rate constant ( $k_1$ ) is lower than that for vinyl alcohol + Cl channel ( $k_2$ ) at 300K.  $k_1$  increases to its peak value  $10^{10.425}$  at 500K then decreases with increasing temperature.

A plot of rate constants versus  $1000/T$  at 760 torr for  $\beta$ -addition product channels is shown in Figure IIB. 6. The stabilization channel dominates the reaction in the temperature range 300-1200K. Reverse reaction, dissociation to vinyl chloride + OH, increases and dominates stabilization above 1200K. Above 2000K, the unimolecular reaction  $H + CHOHCHCl$  and  $CH_2O + CH_2Cl$  is predicted to become important. Calculated apparent rate parameters to the specific product channels are also listed in Table IIA. 6.

Figure IIB. 7 illustrates a plot of rate constant to the major channels from both addition and abstraction reaction channels over the temperature range 300-2000 K for comparison with experimental data at 760 torr. At low temperature, the  $\beta$ -addition channel  $k_9$  dominates the reaction, as reported by Liu et al.<sup>3</sup> At high temperature, however, we calculate that reverse reaction  $k_2$  — dissociation to vinyl chloride + OH (experimentally observed as reduced reaction rate or negative activation energy) dominates over stabilization. A small, near constant (15%), fraction of the reactions proceed via  $\alpha$ -addition to products  $C_2H_3OH + Cl$ .

The abstraction reactions dominate above 1100K, also shown in Figure IIB. 7. The rate constants of two abstraction channels calculated by Transition-State-Theory are also shown. The calculated total abstraction rate constant ( $k_a + k_b$ ) are consistent with the observed experimental data of Liu et al.<sup>3</sup>. The calculation indicates that total abstraction reaction becomes important above 1400 K, while Liu et al.<sup>3</sup> report that it dominates above 723 K. The total rate constant — addition plus abstraction, is shown to be in good agreement with experimental data over the low temperature range 300 to 600K at 760 torr.

Figure IIB. 8 shows the rate constants versus pressure at 300 K for all addition reaction channels. The  $\beta$ -addition channel ( $k_9$ ) is at least 2 orders of magnitude faster than other reactions and it dominates the reaction as suggested by others<sup>1-3</sup>.

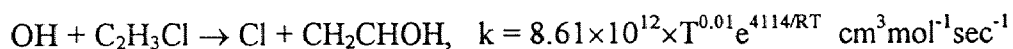
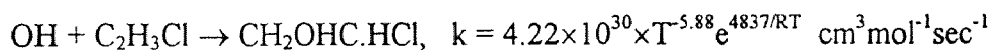
Figure IIB. 9 shows a comparison of the calculated results for both addition reactions with the experimental data of other researchers<sup>1-3</sup>. At room temperature the  $\beta$ -addition reaction channel ( $k_9$ ) dominates all other channels and it almost equals to  $k_{\text{total}}$  over the pressure range of 0.076 to 7600 torr. Howard<sup>1</sup> extrapolated his experimental data (0.7 to 7 torr) for the reaction of OH radicals with  $\text{C}_2\text{H}_3\text{Cl}$  using a curved Lindemann plot and estimated a value for  $k \approx 4.20 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in the high pressure limit (ca. 100 torr) while Perry et al.<sup>2</sup> proposed that their work at 50 torr were at the high pressure limit and estimated a value of  $k \approx 3.97 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . The model indicates from Figure IIB. 9 that the results of both the Perry et al.<sup>2</sup> and Liu et al.<sup>3</sup> research groups is near the high pressure limit. The rate constant increases only 5% from 7 torr to 760 torr as illustrated in Figure IIB. 9.

MOPAC6/PM3-calculated TS's were used to obtain all the rate constants except for that of  $\beta$ -addition of  $\text{OH} + \text{C}_2\text{H}_3\text{Cl}$  ( $k_9$ ) which is from the value of Liu et al.<sup>3</sup>. The transition state structure and two parameter rate constant of  $k_9$  is shown in Figure IIB. 4 and Table IIA. 5, respectively. Although the structure seems reasonable (Figure IIB. 4), the QRRK calculation is not consistent with the experiments: it shows a positive temperature dependence of  $k_9$ . The experimental data from Liu et al.<sup>3</sup> was used in this model instead of the TS in PM3 derived rate constant. There is future work that can be done to refine and improve/complete this modeling: (1) Ab initio method or density function calculations (see page 520 of ref. 34.) at high levels are suggested to perform to

determined the thermodynamic properties and parameters ( $A$ ,  $n$  and  $E_a$ ) of rate constants from the transition state structures and properties; (2) All possible reaction channels are included into this system: 1,2-OH and/or Cl shift in both  $\alpha$ - and  $\beta$ -addition subsystems.

## 5.2 Conclusion

The addition reactions of vinyl chloride with hydroxyl radical were analyzed using PM3 transition states and chemical activation formalism based on a multi-frequency Quantum RRK Theory for  $k(E)$  and a modified strong collision approach of Gilbert et al.<sup>4</sup> for fall-off. Rate constants and reaction paths were predicted versus temperature and pressure and were compared with experimental data where available. The two abstraction paths were analyzed using an Evans-Polanyi relation for activation energy and Transition-State-Theory for Arrhenius  $A$  factors. The calculations serve as useful estimates for rate constants and reaction paths in applications of combustion and atmospheric modeling (pressure and temperature), where experimental data are not available. We evaluated and recommended rate constants over wide pressure and temperature range for the addition and abstraction reaction at the two distinct carbon atom sites on vinyl chloride. Rate constant expressions for the primary addition channels at 760 torr are:



Extension of these analysis technique should allow reasonable estimation of the expected product distributions for a variety of addition reactions of hydroxyl radicals to other halogenated ethylenes.

**Table IIA. 6** Apparent rate constants of OH + C<sub>2</sub>H<sub>3</sub>Cl at different pressures

$$k = A \times T^n \times e^{-E_a/RT} \quad \text{units in cm}^3/\text{mol}/\text{sec}, E_a \text{ in kcal/mol}$$

OH + C<sub>2</sub>H<sub>3</sub>Cl at 7600 torr

Reaction	A	n	E <sub>a</sub>	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	2.32E+24	-3.99	5.877	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	1.43E+14	-0.31	5.714	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	3.97E+03	2.79	5.736	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	1.60E+09	0.98	5.264	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	2.73E+05	2.11	5.629	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	2.59E+00	2.17	11.278	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	7.30E-03	3.98	11.812	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	6.45E+02	2.65	12.549	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	3.67E+22	-3.29	2.551	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	1.03E+14	2.68	7.943	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	5.74E+12	-1.26	16.104	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O + CH <sub>2</sub> Cl	7.90E+06	1.61	16.849	

OH + C<sub>2</sub>H<sub>3</sub>Cl at 760 torr

Reaction	A	n	E <sub>a</sub>	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	2.82E+22	-3.77	4.379	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	8.61E+14	0.01	4.114	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	7.03E+01	3.26	4.003	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	5.38E+07	1.37	3.588	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	5.12E+03	2.58	3.889	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	7.16E-03	2.60	9.948	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	1.67E-04	4.43	10.46	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	1.73E+01	3.08	11.216	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	4.22E+30	-5.88	4.837	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	2.98E+12	0.15	9.566	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	1.71E+18	-3.21	16.858	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O + CH <sub>2</sub> Cl	3.41E+12	-0.11	17.239	



OH + C<sub>2</sub>H<sub>3</sub>Cl at 76 torr

Reaction	A	n	Ea	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	3.09E+20	-3.50	3.658	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	8.74E+11	0.28	3.390	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	7.18E+00	3.54	3.319	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	5.22E+06	1.66	2.868	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	5.14E+02	2.86	3.208	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	2.53E-04	2.73	9.633	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	5.82E-05	4.56	10.146	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	6.10E+00	3.21	10.901	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	8.42E+37	-8.31	6.577	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	1.23E+16	-0.99	9.243	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	9.56E+17	-3.50	15.649	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O+CH <sub>2</sub> Cl	3.64E+12	-0.19	15.771	

OH + C<sub>2</sub>H<sub>3</sub>Cl at 7.6 torr

Reaction	A	n	Ea	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	2.17E+19	-3.46	3.551	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	6.11E+11	0.33	3.284	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	5.13E+00	3.58	3.223	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	3.66E+06	1.70	2.764	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	3.66E+02	2.90	3.111	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	2.24E-05	2.74	9.597	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	5.14E-05	4.58	10.11	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	5.39E+00	3.23	10.864	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	4.89E+42	-10.04	7.211	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	9.44E+14	-0.72	7.377	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	2.45E+15	-3.06	14.29	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O+CH <sub>2</sub> Cl	6.42E+10	0.30	14.377	

OH + C<sub>2</sub>H<sub>3</sub>Cl at 0.76 torr

Reaction	A	n	Ea	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	2.09E+18	-3.45	3.539	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	5.88E+11	0.33	3.273	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	4.95E+00	3.58	3.213	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	3.52E+06	1.70	2.753	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	3.53E+02	2.90	3.101	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	2.21E-06	2.75	9.593	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	5.08E-05	4.58	10.106	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	5.33E+00	3.23	10.864	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	2.64E+44	-10.89	6.711	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	5.43E+12	-0.09	5.726	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	8.01E+13	-2.92	13.95	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O+CH <sub>2</sub> Cl	2.06E+10	0.44	14.042	

OH + C<sub>2</sub>H<sub>3</sub>Cl at 0.076 torr

Reaction	A	n	Ea	remark
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CH <sub>2</sub> C.Cl	1.06E+07	2.0	5.31	α-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → H <sub>2</sub> O + CHClC.H	1.59E+07	2.0	6.2	β-abstraction
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClOHC.H <sub>2</sub>	2.08E+17	-3.45	3.538	α-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>2</sub> CHOH	5.86E+11	0.33	3.272	
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CH <sub>2</sub> COHCl	4.93E+00	3.58	3.212	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + C.H <sub>2</sub> CHO	3.51E+06	1.71	2.752	
OH + C <sub>2</sub> H <sub>3</sub> Cl → HCl + CH <sub>2</sub> C.OH	3.52E+02	2.91	3.100	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO.CH <sub>3</sub>	2.21E-07	2.75	9.593	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CHClO + CH <sub>3</sub>	5.07E-05	4.58	10.106	
OH + C <sub>2</sub> H <sub>3</sub> Cl → Cl + CH <sub>3</sub> CHO	5.32E+00	3.23	10.86	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> OHC.HCl	4.62E+43	-11.01	5.496	β-addition
OH + C <sub>2</sub> H <sub>3</sub> Cl → H + CHClCHOH	8.86E+11	0.13	5.218	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O.CH <sub>2</sub> Cl	6.98E+12	-2.91	13.91	
OH + C <sub>2</sub> H <sub>3</sub> Cl → CH <sub>2</sub> O+CH <sub>2</sub> Cl	1.80E+10	0.46	14.003	

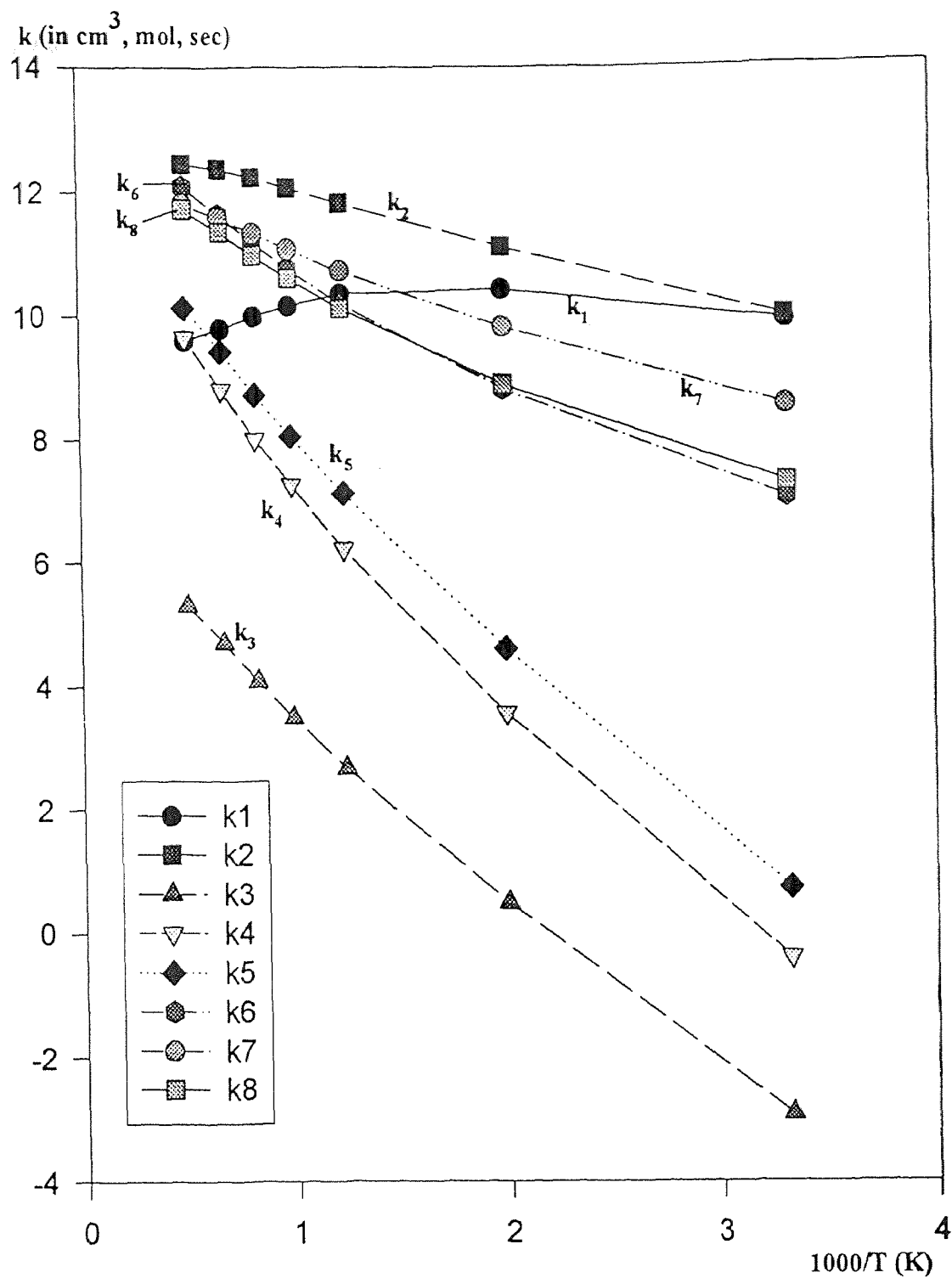


Figure IIB. 5 Rate constants vs. temperatures for  $\alpha$ -addition of  $\text{OH} + \text{C}_2\text{H}_3\text{Cl}$  at 760 torr

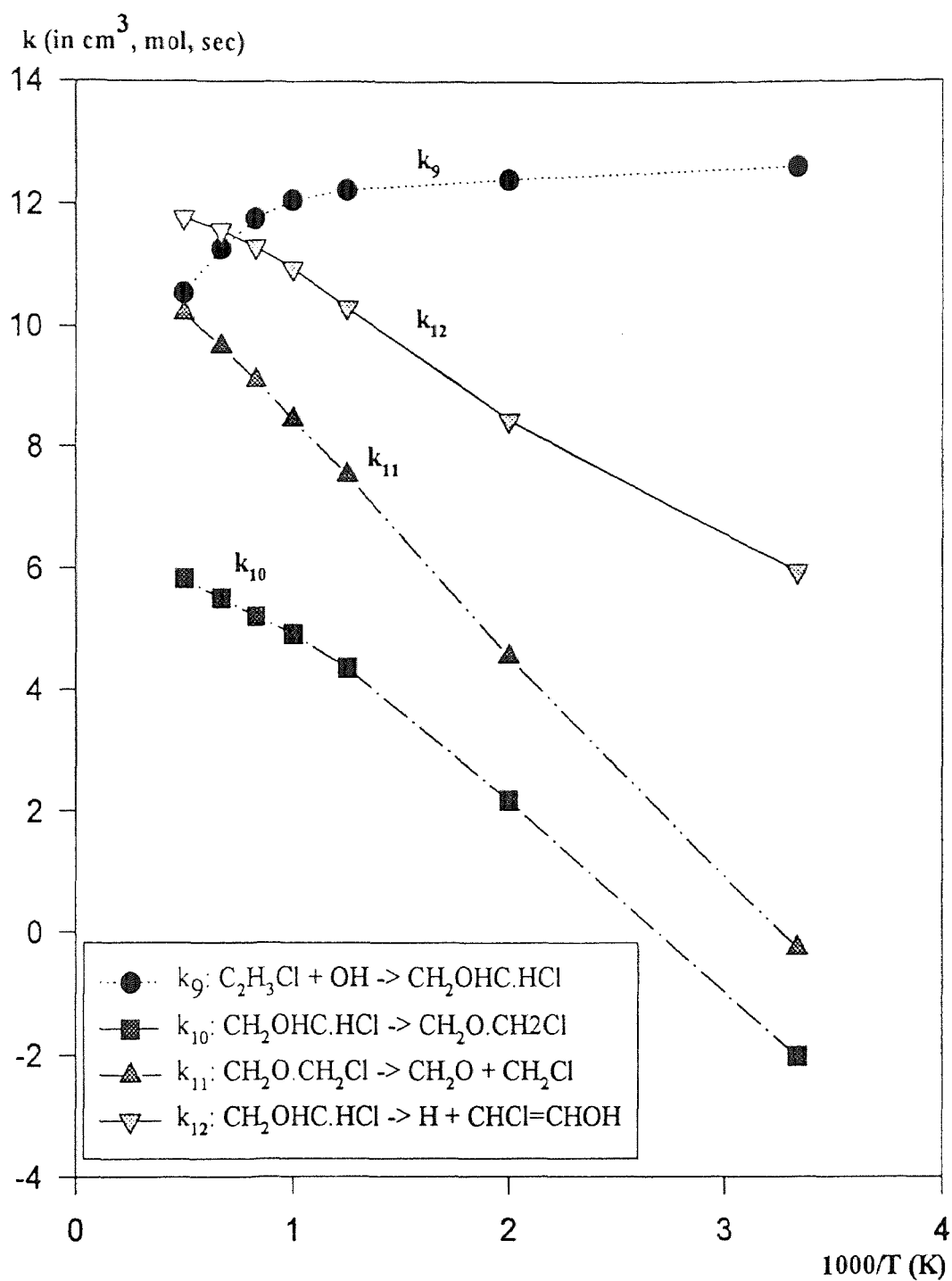


Figure IIB. 6 Rate constants vs. temperatures for  $\beta$ -addition of  $\text{OH} + \text{C}_2\text{H}_3\text{Cl}$  at 760 torr

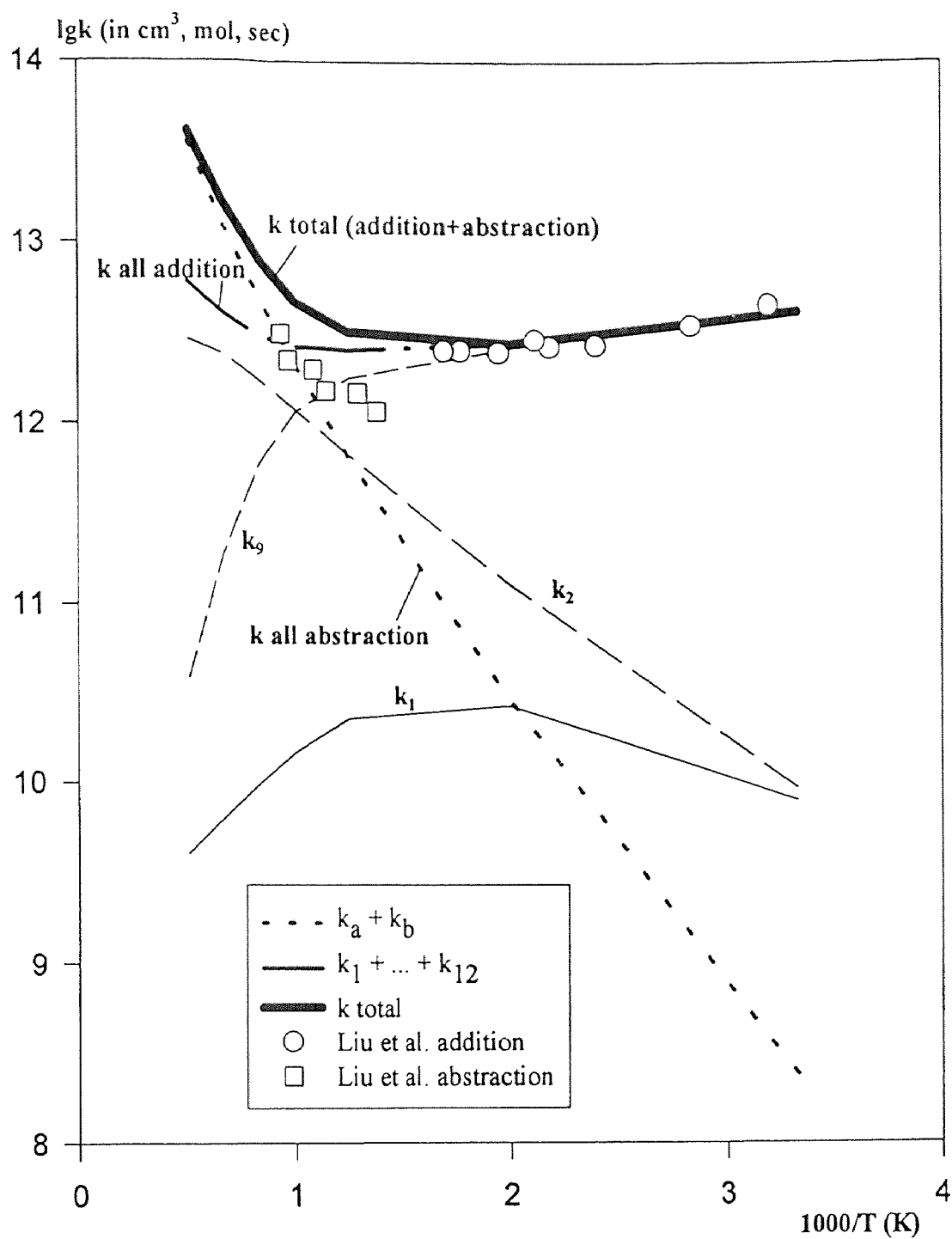


Figure IIB. 7 Comparison of model with experiments for temperature dependence of rate constants at 760 torr

$\lg k$  (in  $\text{cm}^3, \text{mol}, \text{sec}$ )

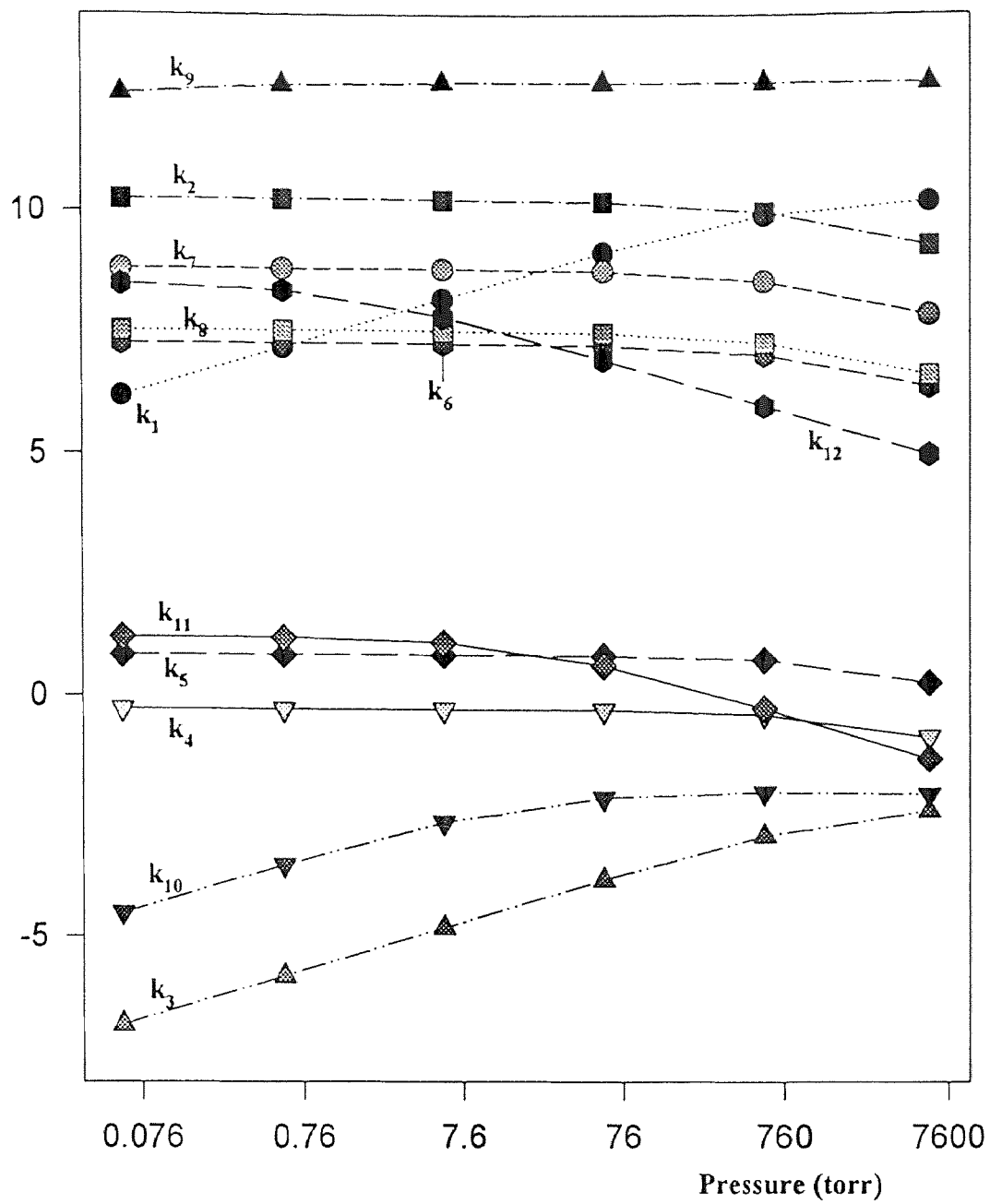


Figure IIB. 8 Rate constants vs. pressures for  $\text{OH} + \text{C}_2\text{H}_3\text{Cl}$  at 300K

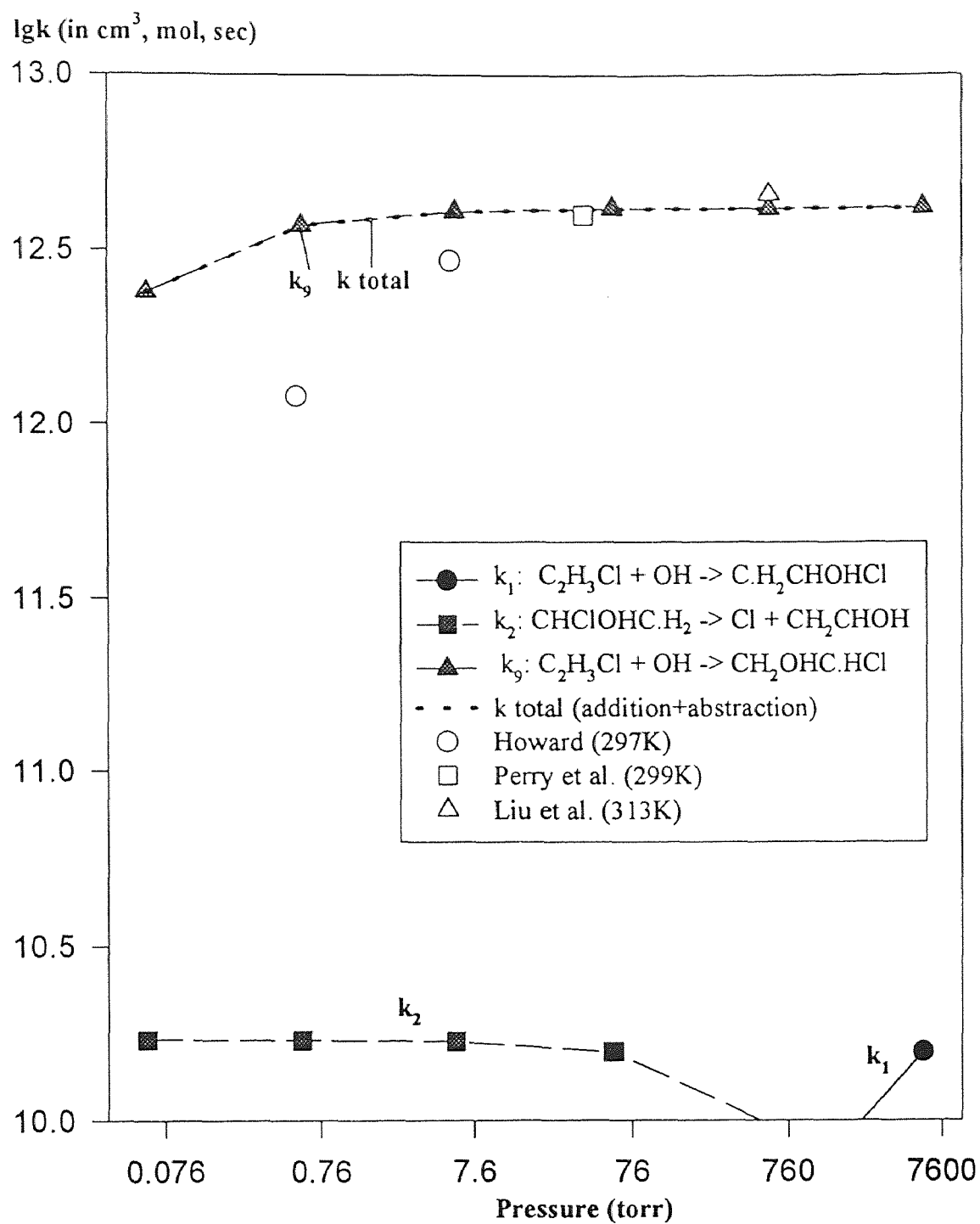


Figure IIB. 9 Comparison model with experiments for pressure dependence of rate constants at room temperature

APPENDIX  
(FOR PART I)

THERM FILES OF CHLOROCARBONS

SPECIES

C2H5CL

Thermo estimation for molecule

C2H5CL

C2H5CL

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - C/C/H3 - 1

2 - C/C/CL/H2 - 1

Hf S Cp 300 400 500 600 800 1000 1500

-27.00 66.26 14.93 18.38 21.48 24.10 28.17 31.24 .00

CPINF = 42.72

NROTORS: 1

SYMMETRY 3

CREATION DATE: 3/13/97

ENDSPECIES

SPECIES

CH3CHCL2

Thermo estimation for molecule

CH3CHCL2

C2H4CL2

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - C/C/H3 - 1

2 - C/C/CL2/H - 1

Hf S Cp 300 400 500 600 800 1000 1500

-31.10 73.05 18.40 21.82 24.67 27.15 30.69 33.35 .00

CPINF = 42.72

NROTORS: 1

SYMMETRY 3

CREATION DATE: 3/13/97

ENDSPECIES

SPECIES

CH2LCH2L

Thermo estimation for molecule

CH2LCH2L

C2H4CL2

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity



1 - C/C/CL/H2 - 2  
 2 - INT/CL2 - 1  
 Hf S Cp 300 400 500 600 800 1000 1500  
 -31.05 73.84 18.23 21.54 24.39 26.70 30.25 32.94 .00  
 CPINF = 42.72  
 NROTORS: 1  
 SYMMETRY 2  
 CREATION DATE: 3/13/97  
 ENDSPECIES

## SPECIES

CH3CCL3

Thermo estimation for molecule

CH3CCL3

C2H3CL3

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - C/C/H3 - 1

2 - C/C/CL3 - 1

Hf S Cp 300 400 500 600 800 1000 1500  
 -33.90 76.55 22.02 25.70 28.65 30.89 34.08 35.98 .00  
 CPINF = 42.72

NROTORS: 1

SYMMETRY 9

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

CH2LCHL2

Thermo estimation for molecule

CH2LCHL2

C2H3CL3

UNITS:KCAL

GROUPS 3

Gr # - GROUP ID - Quantity

1 - C/C/CL/H2 - 1

2 - C/C/CL2/H - 1

3 - INT/CL3 - 1

Hf S Cp 300 400 500 600 800 1000 1500  
 -34.00 81.43 21.53 24.85 27.39 29.55 32.58 35.05 .00  
 CPINF = 42.72

NROTORS: 1

SYMMETRY 1

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

1112CLEA

Thermo estimation for molecule

1112CLEA

C2H2CL4

UNITS:KCAL

GROUPS 3

Gr # - GROUP ID - Quantity

1 - C/C/CL/H2 - 1

2 - C/C/CL3 - 1

3 - INT/CL4 - 1

Hf S Cp 300 400 500 600 800 1000 1500

-35.16 84.46 24.62 28.29 31.07 33.17 36.11 37.68 .00

CPINF = 40.73

NROTORS: 3

SYMMETRY 3

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

1122CLEA

Thermo estimation for molecule

1122CLEA

C2H2CL4

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - C/C/CL2/H - 2

2 - INT/CL4 - 1

Hf S Cp 300 400 500 600 800 1000 1500

-36.46 86.36 24.47 27.85 30.28 32.48 35.24 37.16 .00

CPINF = 42.72

NROTORS: 1

SYMMETRY 2

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

C2HCL5

Thermo estimation for molecule

C2HCL5

C2HCL5

UNITS:KCAL

GROUPS 3

Gr # - GROUP ID - Quantity

1 - C/C/CL2/H - 1

2 - C/C/CL3 - 1

3 - INT/CL5 - 1

Hf S Cp 300 400 500 600 800 1000 1500  
 -34.00 90.95 28.49 31.86 34.21 36.02 38.20 39.79 .00  
 CPINF = 42.72

NROTORS: 1  
 SYMMETRY 3  
 CREATION DATE: 3/13/97  
 ENDSPECIES

## SPECIES

C2CL6

Thermo estimation for molecule

C2CL6 C2CL6

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - C/C/CL3 - 2

2 - INT/CL6 - 1

Hf S Cp 300 400 500 600 800 1000 1500  
 -34.06 94.77 32.72 36.16 38.35 39.76 41.39 42.42 .00  
 CPINF = 42.72

NROTORS: 1  
 SYMMETRY 18  
 CREATION DATE: 3/13/97  
 ENDSPECIES

## SPECIES

C2H3CL

Thermo estimation for molecule

C2H3CL C2H3CL

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - CD/CL/H - 1

2 - CD/H2 - 1

Hf S Cp 300 400 500 600 800 1000 1500  
 5.06 63.01 13.00 15.56 17.81 19.70 22.37 24.37 .00  
 CPINF = 31.79

SYMMETRY 1  
 CREATION DATE: 3/13/97  
 ENDSPECIES

## SPECIES

CH2CCL2

Thermo estimation for molecule

CH2CCL2 C2H2CL2

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - CD/CL2 - 1

2 - CD/H2 - 1

Hf	S	Cp	300	400	500	600	800	1000	1500	
.50	67.00	16.07	18.78	20.84	22.42	24.70	26.28		.00	

CPINF = 31.79

SYMMETRY 2

CREATION DATE: 3/13/97

ENDSPECIES

SPECIES

ZC2H2CL2

Thermo estimation for molecule

ZC2H2CL2

C2H2CL2

UNITS:KCAL

GROUPS 3

Gr # - GROUP ID - Quantity

1 - CD/CL/H - 2

2 - INT/CD/CL2 - 1

3 - CIS/CL/CL - 1

Hf	S	Cp	300	400	500	600	800	1000	1500	
.00	69.25	16.26	18.97	21.08	22.72	24.79	26.17		.00	

CPINF = 31.79

SYMMETRY 2

CREATION DATE: 3/13/97

ENDSPECIES

SPECIES

EC2H2CL2

Thermo estimation for molecule

EC2H2CL2

C2H2CL2

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - CD/CL/H - 2

2 - INT/CD/CL2 - 1

Hf	S	Cp	300	400	500	600	800	1000	1500	
.30	70.63	16.45	19.01	21.05	22.68	24.79	26.20		.00	

CPINF = 31.79

SYMMETRY 1

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

C2HCL3

Thermo estimation for molecule

C2HCL3

C2HCL3

UNITS:KCAL

GROUPS 3

Gr # - GROUP ID - Quantity

1 - CD/CL2 - 1

2 - CD/CL/H - 1

3 - INT/CD/CL3 - 1

Hf S Cp 300 400 500 600 800 1000 1500

-2.22 77.67 19.26 21.80 23.67 25.06 26.94 28.11 .00

CPINF = 31.79

SYMMETRY 1

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

C2CL4

Thermo estimation for molecule

C2CL4

C2CL4

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - CD/CL2 - 2

2 - INT/CD/CL4 - 1

Hf S Cp 300 400 500 600 800 1000 1500

-3.15 81.47 22.73 25.10 26.72 27.86 29.28 30.02 .00

CPINF = 31.79

SYMMETRY 4

CREATION DATE: 3/13/97

ENDSPECIES

## SPECIES

C2HCL

Thermo estimation for molecule

C2HCL

C2HCL

UNITS:KCAL

GROUPS 2

Gr # - GROUP ID - Quantity

1 - CT/H - 1

2 - CT/CL - 1

Hf S Cp 300 400 500 600 800 1000 1500

51.42 58.10 13.18 14.39 15.19 15.87 16.87 17.56 .00

CPINF = 19.87

```

SYMMETRY      1
CREATION DATE: 3/13/97
ENDSPECIES
SPECIES
C2CL2
Thermo estimation for molecule
C2CL2                      C2CL2
UNITS:KCAL
GROUPS  2
  Gr # - GROUP ID - Quantity
    1 - CT/CL      - 2
    2 - INT/CL2    - 1
Hf  S  Cp 300  400  500  600  800 1000 1500
50.89 64.58 16.55 17.26 17.63 18.08 18.75 19.20 .00
      CPINF = 19.87
SYMMETRY      2
CREATION DATE: 3/13/97
ENDSPECIES

```

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